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ACCUMULATION OF METALS IN THE NORTH-EASTERN GULF OF FINLAND, BALTIC SEA

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Tiivistelmä/Referat – Abstract

The Baltic Sea is a vulnerable marine environment and susceptible to pollution. The situation is especially severe in the Gulf of Finland due to a large catchment area compared to the size of the Gulf. The north eastern Gulf of Finland has been described as one of the most contaminated areas of the entire Baltic Sea, with extensive pollution load via river Kymi in the past. Still today, the currents bring contaminants from the eastern part of the Gulf – the Neva estuary and the Bay of Viborg.

The concentrations of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Hg, Pb, Bi and La were studied in the surface sediments and three GEMAX cores. The vertical distribution revealed the temporal change in the metal accumulation. The spike in the Cs concentration, indicating the Chernobyl disaster in 1986, enabled the estimation of the accumulation of studied elements over time. The horizontal distribution maps based on the concentrations in the surface sediments enabled the discovery of the sites with most intense metal accumulation. Correlation coefficients showed the effect of carbon and sediment grain size in the distribution of metals. The comparison of the metal concentrations to the natural background levels and the Canadian sediment quality guidelines (SQGs) enabled the estimation of the degree of contamination of the area.

The metal concentrations have declined during the last decades in the north eastern Gulf of Finland, indicating lower contamination input towards present day. However, in the oxidized Ravijoki core, the decline was not that obvious, probably due to metal scavenging by Fe and Mn oxides and bioturbation. The regional metal distribution was strongly affected by the grain size and carbon – most metals showed high positive correlations with carbon and finer sediment fraction. Mn was an exception, showing negative correlations with both carbon and clay, probably due to the Mn reduction at sites with high organic matter accumulation. The regional distribution pattern suggested main Cd pollution arriving from the eastern part of the Gulf. The distribution of Hg, Mo, Cu and Zn also suggested a possible source in the east. High concentrations of Hg, Pb and Cu were discovered in the outlets of river Kymi.

According to the Canadian SQGs, the sediments in the north-eastern Gulf of Finland were contaminated. The situation is especially severe in the case of Zn – the higher reference value PEL, above which adverse biological effects frequently occur, was exceeded even in the oxidized Ravijoki sediments. The highest concentrations of the elements with defined SQGs (Cd, Cr, Zn, Cu, Hg, Pb and As) exceeded the lower reference values in the surface sediments, indicating that all these metals could, at least locally, pose a severe threat to benthic species.

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Tiivistelmä/Referat – Abstract

Itämeri on hauras, saastumiselle altis merellinen ympäristö. Tilanne saastumisen suhteen on erityisen vakava Suomenlahdella, jossa valuma-alue on laaja lahden kokoon nähden. Suomenlahden koillisosaa on luonnehdittu yhdeksi koko Itämeren saastuneimmista osista, erityisesti aiemmin Kymijoen kautta kulkeutuneiden saasteiden takia. Nykyään virtaukset tuovat saasteita erityisesti lahden itäosista, kuten Nevanjoen suulta ja Viipurinlahdelta.

Vanadiumin, kromin, mangaanin, raudan, koboltin, nikkelin, kuparin, sinkin, arseenin, molybdeenin, antimonin, elohopean, lyijyn, vismutin ja lantaanin pitoisuuksia tutkittiin sekä pintasedimenteistä että GEMAX-kairanäytteistä. Kairausprofiilin vertikaalinen jakautuminen paljasti muutoksen sedimentin kerrostumisessa ajan myötä. Tshernobylin katastrofista vuodelta 1986 peräisin oleva cesiumin pitoisuushuippu mahdollisti sedimentin kerrostumisen ajoituksen. Pintasedimenttien metallipitoisuuksiin perustuvien pitoisuuskarttojen perusteella pystyttiin osoittamaan ne alueet, joille on kerrostunut eniten metalleja. Korrelaatiokertoimet osoittivat orgaanisen aineksen ja sedimentin raekoon vaikutukset metallien esiintyvyyteen. Metallien pitoisuuksien vertaaminen taustapitoisuuksiin ja kanadalaisiin sedimentin laatusuosituksiin mahdollistivat kontaminaatioriskin arvioinnin tutkimusalueella.

Metallien pitoisuudet ovat laskeneet viime vuosikymmenten aikana koillisella Suomenlahdella, mikä viittaa aiempaa vähäisempiin päästöihin. Kuitenkin happipitoisessa Ravijoen kairanäytteessä pitoisuuksien lasku ei ollut niin selkeää, mikä luultavasti johtuu metallien sitoutumisesta rauta- ja mangaanioksideihin sekä bioturbaatiosta. Alueelliseen metallien esiintyvyyteen vaikutti vahvasti raekoko, sekä hiili – useimmat metallit korreloivat positiivisesti hiilen ja hienon sedimenttifraktion kanssa. Mangaanin korrelaatio hiilen ja saven kanssa oli poikkeuksellisesti negatiivinen. Negatiivinen korrelaatio todennäköisesti johtuu mangaanin pelkistymisestä paikoilla, joilla kerrostuu paljon orgaanista ainesta. Kadmiumin pitoisuuskartta viittaa siihen, että suurin osa kadmiumista saapuu tutkimusalueelle Suomenlahden itäosista. Myös elohopean, molybdeenin, kuparin ja sinkin pitoisuuskartat viittaavat mahdolliseen lähteeseen idässä. Korkeita elohopea-, lyijy- ja kuparipitoisuuksia löytyi myös Kymijoen suulta.

Kanadalaisten sedimentin laatusuositusten perusteella koillisen Suomenlahden sedimentit ovat kontaminoituneita. Tilanne on erityisen vakava sinkin suhteen – ylempi raja-arvo PEL, jonka ylittyessä biologisia haittavaikutuksia usein esiintyy, ylittyi jopa happipitoisissa Ravijoen sedimenteissä. Niiden aineiden, joille on määritelty sedimentin laatusuositukset (kadmium, kromi, sinkki, kupari, elohopea, lyijy ja arseeni), korkeimmat pitoisuudet ylittivät alemman raja-arvon pintasedimenteissä. Nämä metallipitoisuudet voivat aiheuttaa kanadalaisten laatusuositusten mukaan ainakin paikallisesti vakavan uhan pohjaeliöstölle.

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Contents

1. INTRODUCTION

The Baltic Sea is an especially vulnerable marine environment and is susceptible to pollution due to many reasons (HELCOM 2010a). The sea is relatively shallow (Leppäranta and Myrberg 2009), the residence time of water is long, and the drainage area is very large (Figure 1), approximately 85 million people inhabiting the drainage area (Leppäranta and Myrberg 2009, HELCOM 2010a).

The Baltic Sea faces many environmental challenges these days. The anthropogenic impact is seen as increased loads of nutrients (HELCOM 2014) and various pollutants, including heavy metals (HELCOM 2010a), affecting water quality, biota and the sediments of the sea. Other pressures include marine litter, underwater sound and non-indigenous species, loss of species by fishing and hunting and the disturbance of the seabed (HELCOM 2018a).

Figure 1. The drainage area of the Baltic Sea is very large. The sea is surrounded by nine countries with approximately 85 million people living on the drainage area (Modified HELCOM 2018, ArcGIS Light Canvey map).

Heavy metals accumulated in the marine animals can cause severe health risks for humans and are inedible (HELCOM 2007, HELCOM 2010a). Metals also deteriorate the health of marine animals and their ability to reproduce (HELCOM 2007). Many heavy metals have been found to be toxic to organisms even as small doses; Cd and Pb negatively affect the liver function, whereas Hg cumulates in the muscle tissue (HELCOM 2010a). High metal concentrations, especially high concentrations of Cd, can harm bones and high Hg and Pb concentrations have harmful effects on neurotransmitters (Lahermo et al. 1996, HELCOM 2010a). Hg concentrations measured in fish muscle exceeded the threshold values in almost all the Baltic Sea, only in Arkona basin and some coastal areas of Sweden and Denmark the concentrations were not above the threshold limits (HELCOM 2018a).

Even though external inputs of nutrients have decreased since the 1980's, almost the entire Baltic Sea is still affected by eutrophication (HELCOM 2014, HELCOM 2018a). Increasing loads of nutrients cause eutrophication, which in turn enhances algal growth. More intense decomposition of organic matter occurs at the sea bottom because of the increased growth of algae. This action consumes oxygen and eventually leads to oxygen depletion at the bottom of the sea, creating anoxic conditions (HELCOM 2014, Ryan 2014). These conditions favour the release of certain metals from the sediment back to the water column (Leivuori 1998, Vallius et al. 2011). Under anoxic conditions, the already accumulated P in the sediments, too, is dissolved, which together with the long residence time of water makes the recovery from the eutrophic state extremely slow (HELCOM 2014).

1.1. Oceanography of the Baltic Sea and Gulf of Finland

The Baltic Sea is located in a relatively small and shallow basin with surface area of 392,978 km² and volume of 21,205 km³. The mean depth of the sea is only 54 metres (Leppäranta and Myrberg 2009), and more than one third of the sea does not reach the depth of 30 metres, making the total volume small in comparison to the total area (HELCOM 2018a). The Landsort Deep between the city of Stockholm and the island of Gotland is the deepest part of the sea, reaching the depth of 459 metres (Leppäranta and Myrberg 2009).

The Gulf of Finland is the eastern part of the Baltic Sea. The Gulf is a relatively large estuarine basin compared to the other sub-basins of the Baltic Sea with a volume of 1103 km³, which is circa 5% of the total volume of the sea, whereas the drainage area of 420 990 km² makes almost 20% of the total drainage area of the sea (Alenius et al. 1998). There is no sill distinguishing the Gulf of Finland from

the Gotland Sea (Leppäranta and Myrberg 2009, Alenius et al. 2016). The southern Estonian coast is rather steep with only a few islands, whereas the northern Finnish coast is much shallower and characterized with an irregular coastline and many small islands (Alenius et al. 1998, Leppäranta and Myrberg 2009). The change in landscape is due to the boundary between the crystalline bedrock in the northern coast and sedimentary rocks in the south, where these younger rocks smooth the landscape (Kotilainen et al. 2016). The Gulf of Finland has a mean depth of 37 metres with a relatively deep (> 60 meters) central part (Kotilainen et al. 2016), but a very shallow eastern part (Alenius et al. 1998). In general, the deepest areas of the Gulf are 80 – 100 metres and are found in the western and southern parts (Leppäranta and Myrberg 2009, Kotilainen et al. 2016). The Paldiski Deep located in the Estonian coast just outside the town of Paldiski, reaches the depth of 123 metres (Leppäranta and Myrberg 2009), and another deep (138 metres) is found west of the Paldiski Deep, north of the Osmusaar Island (Kotilainen et al. 2016). Deep basins and underwater canyons appear in the eastern parts of the Gulf, too (Kotilainen et al. 2016).

The sedimentation basins in the Gulf of Finland are relatively small, and the largest basins are in the southern parts of the Gulf, near the Estonian coast (Leivuori and Vallius 2004), and the central parts of the Gulf (Kaskela et al. 2016). Currently, one-third of the seafloor of the Gulf can be considered as a sediment accumulation area (Kaskela et al. 2012).

The Baltic Sea is connected to the North Sea only through the narrow Danish straits (Leppäranta and Myrberg 2009, HELCOM 2010b). The waters of the of the Baltic Sea are characterized by a low mean salinity of around 7 ‰, which is only one-fifth of the salinity of normal ocean water (Leppäranta and Myrberg 2009). The salinity decreases from the Danish straits to the most remote basins (HELCOM 2010b), where the water is diluted by the freshwater inflow from the rivers (Leppäranta and Myrberg 2009). The lowest salinities in the Baltic Sea are measured in the most eastern parts of the Gulf of Finland and northern parts of the Gulf of Bothnia, Bothnian Bay (HELCOM 2010b). The Gulf of Finland receives most of its freshwater from the River Neva in the easternmost part of the Gulf (Alenius et al. 2016). Other large fluxes of freshwater arrive through river Kymi on the northern coast and through rivers Narva and Luga on the southern coast of the Gulf (Alenius et al. 1998). Due to the large inflow of freshwater from river Neva, the salinity is permanently lower in the eastern parts compared to the western parts of the Gulf – the salinity of the surface water gradually increases from 0 ‰ measured at the mouth of Neva to the values of 6 – 6,5 ‰ in the western parts of the Gulf (Leppäranta and Myrberg 2009, Alenius et al. 2016). The same trend is observed in waters of the bottom layer (Leppäranta and Myrberg 2009). In the east, the salinity ranges between 0 – 5 ‰, in the central parts 5 – 8 ‰, and in the west 7 – 9 ‰, occasionally over 10 ‰ (Alenius et al. 2016). The

near-bottom salinity is characterized by seasonality – higher salinities are observed in the summer time, while the salinities lower towards the winter season (Alenius et al. 2016).

In general, the amount of freshwater arriving from the catchment area to the Baltic Sea is larger than the amount of the saline water from the North Sea, which makes the water statue strongly stratified (Schinke and Matthäus 1998, HELCOM 2010b). In the Gulf of Finland, salinity is the major factor in determining the stratification of the water column, the seasonal summer-time thermocline playing a smaller role (Alenius et al. 2016). The halocline weakens the vertical convection, which has a negative impact on the oxygen condition of the seafloor: many times, hypoxic, or even anoxic, conditions prevail (Leppäranta and Myrberg 2009). The halocline is less strong in the eastern parts of the Gulf, and especially on shallow coastal areas, the permanent halocline is missing due to effective mixing by strong winds and the large freshwater input through River Neva (Alenius et al. 2016).

The inflow of the saline water is crucial for the Baltic Sea, because this is the only way to bring oxygen to the deep-sea basins of the Baltic due to strong stratification of the water statue (Leppäranta and Myrberg 2009, Mohrholz et al. 2015). However, the normal inflow of oceanic water from the North Sea is not strong enough to renew the waters in the deeps of the Baltic Sea (Leppäranta and Myrberg 2009). From time to time, strong and highly saline *Major Baltic Inflows* (MBI) bring oxygen-rich water to the Baltic Sea basin, and this improves the oxygen conditions of the deeps (Leppäranta and Myrberg 2009, HELCOM 2010b). The most recent MBI's occurred in 1993, 2003, 2014, 2015 and 2016. The MBI in 2014 arrived in the Baltic Sea after long waiting, and this was one of the strongest known MBI's of the history of the Baltic Sea (Mohrholz et al. 2015, Feistel et al. 2016). The 2014 MBI was followed by less strong MBI's in November 2015 and January-February 2016 (Feistel et al. 2016).

Water, as well as the substances from the large drainage area, can reside in the waters of the Baltic Sea for decades (HELCOM 2010b); the entire water mass is estimated to renew in 50 years (Leppäranta and Myrberg 2009). It has been estimated that the concentrations of harmful substances in the Baltic Sea can be even 20 times higher than those in the waters of the Atlantic Sea (HELCOM 2007, HELCOM 2010a).

In stratified waters, like in the case of the Baltic Sea, the inflowing freshwater settles in the upper layer with matching density and more saline water with higher density sinks to the lower layer. The positive fresh water balance of the Baltic Sea maintains a basic circulation in which the freshwater exits the Baltic in the upper layers near the surface and the more saline ocean waters arrive in the

lower layer (Leppäranta and Myrberg 2009). The currents of the Gulf of Finland are mostly affected by prevailing wind conditions and Earth's rotation which makes the circulation counter-clockwise on Northern hemisphere (Alenius et al. 1998), making the most intense water inflow in the southern coast of the Gulf and outflow on the northern coast (Andrejev et al. 2004). The general circulation description is quite simplified, and the true circulation is more complex and depends on many factors. Even though the prevailing wind conditions are the driving force in the water circulation in the Gulf of Finland, the local short-term wind directions and the density gradients caused by thermohaline variations play a role (Alenius et al. 1998, Andrejev et al. 2004, Leppäranta and Myrberg 2009, Alenius et al. 2016), and instantaneous currents are able to mask the general, long term circulation pattern (Alenius et al. 2016). Also, the topographic changes in the seabed (Alenius et al. 1998) and changes in the sea level affect the circulation (Leppäranta and Myrberg 2009). River runoffs can affect locally on the sea-level, and therefore cause changes in the currents (Leppäranta and Myrberg 2009).

1.2. Heavy metals and their sources

Helsinki Convention (1992) defines as a harmful substance any substance that has a high probability to cause pollution at the sea. These substances do not naturally occur in the sea, or their concentrations have exceeded their natural levels (HELCOM 2007). When harmfulness of a substance is estimated, its' radioactivity, concentration, distribution and impacts on organisms also need to be considered (Helsinki Convention 1992). Many substances have been listed as a harmful substance by Helsinki Convention (1992), including heavy metals and their compounds, many organic compounds, pesticides, oils, compounds of nitrogen and phosphorus and radioactive substances.

Heavy metals are metallic elements with atomic number greater than 20 – the transition group metals, the lanthanides and actinides are all referred as heavy metals. Heavy metals are often called trace metals, since they are not as common as alkali and earth-alkali metals. The sources of heavy metals are both natural and anthropogenic – they occur as small concentrations in different rock types, soils and water (Ryan 2014). The concentrations of naturally occurring heavy metals vary according to the local geology (Vallius et al. 2007, Vallius 2007), and this needs to be considered when assessing the degree of contamination of any area. However, often the elevated concentrations of these elements are due to anthropogenic activities (Ryan 2014), and the human impact is often clearly shown in surface sediments in the bottom of the seas and oceans (Vallius 1999a).

Harmful substances can be transported to the Baltic Sea airborne pathway as atmospheric deposition, waterborne pathways through rivers, direct inputs and ocean dumping (HELCOM 2010a). Atmospheric input is as significant as the others (Krüger 1996) and can even exceed the riverine input (Schneider et al. 2000, HELCOM 2018b). According to Schneider et al. (2000), the atmospheric input is greater than the riverine input for Cd and Pb, but based on the more recent measurements during 2012 – 2014, HELCOM (2018b) states that riverine input is the main pathway for Cd and Pb. For Hg, HELCOM (2018b) has estimated that atmospheric deposition is more important than riverine input. Atmospheric deposition can originate from a great distance: Krüger (1996) estimated that the source of about 25 % of the heavy metal atmospheric deposition in the Baltic Sea is in Western Europe, non-neighbouring countries. The atmospheric deposition of all studied metals Cd, Pb and Hg has reduced since 1990's, with remark reductions in the Pb and Cd deposition compared to that of Hg (HELCOM 2018b).

Most anthropogenically derived heavy metals originate from industrial sources such as mineral and chemical industry, power production, incineration of waste materials, fossil fuel combustion (Krüger 1996, HELCOM 2010a, Liu et al. 2011), oil spills and dissolving of anti-fouling paints (HELCOM 2010a). Heavy metals such as Zn, Cu, Ni, Cr, Co, As, Cd are released from grand metal refining plants, whereas most Pb emissions originate from traffic, and V and Hg emissions from combustion of fossil fuels (Lahermo et al. 1996).

Pollution hot spots in the catchment area of the Baltic Sea have been identified by HELCOM since 1992 (HELCOM 2013). This includes both municipal and industrial waste water treatment, as well as industrial and agricultural sources (HELCOM 2013). Total of 162 hot spots have been identified, of which 110 were deleted from the list by 2013, and the number of remaining active ones was 52 (HELCOM 2013). In the catchment of the Gulf of Finland, five industrial hot spots were deleted by 1998 (Huuska and Forsius 2002) and since that, the metal plating in St Petersburg was deleted in 2008 (HELCOM 2013) and the most combined municipal and industrial hot spots have been deleted by 2016 (HELCOM 2016). The remaining, active hot spots in the Gulf of Finland drainage area include two industrial hot spots, two combined municipal and industrial hot spots, one hazardous waste and one agricultural hot spot in Russia and one power plant in Estonia (HELCOM 2016).

Starting from the beginning of the Industrial Age, radioactive substances have been released to the atmosphere by man. The main causes that have affected the concentration levels of radioactive substances in the Baltic Sea are the nuclear weapon tests by the United States and the Soviet Union in 1950 – 1980, the disaster of the Chernobyl nuclear power plant in April 1986, and the reprocessing

of used nuclear fuel in Europe (HELCOM 2010a). Especially the effects of the Chernobyl disaster are seen clearly in the Baltic Sea sediments (e.g. Zaborska et al. 2014, Moros et al. 2017, Olszewski et al. 2018).

Dumping of dredged sediments and war waste, including chemical munitions at the end of World War II, have affected the marine environment of the Baltic Sea (HELCOM 2010a). Even though the metal concentrations in the dredged sediments do not exceed national levels, the measured metal concentrations in disposed dredged sediments have been high (HELCOM 2010a). Chemical munitions were dumped in 1947 and 1948 in areas south east of Gotland, east of Bornholm and south of the Little Belt (HELCOM 1994). Most warfare agents have been broken down into less toxic forms that dissolve in water, but some compounds dissolve slowly and can be found near the dumpsites (HELCOM 1994). Especially As has been associated to the proximity of chemical munition dumpsites: Beldowski et al. (2016) discovered elevated As concentrations near chemical munition dumpsites. Also, high Hg concentrations are reported at industrial and war waste dumping sites (Leipe et al. 2013).

One of the most important natural sources of heavy metals appears to be acid sulphate soils. Nordmyr et al. (2008) suggested that acid sulphate soils are the source of certain metals (Al, Cd, Co, Cu, Mn, Ni, Zn) in the sediments of the mouth of Vöyrinjoki river in western Finland. When acid sulphate soils are exposed to air, sulphuric acid is formed lowering the pH of the soil, which makes the metals in the soil more soluble. These metals are washed to the river (Nordmyr et al. 2008), and they remain in their soluble form as long as the water remains acid (Nystrand and Österholm 2013). Eventually, the metals reach the sea and begin to precipitate at the river mouth as the acidic water from the river mixes with more neutral water in the sea and consequently, the pH of the water gradually rises (Nystrand and Österholm 2013). Acid sulphate soils are possible sources of metals in the Gulf of Finland, too (Nordmyr et al. 2008).

Contaminated sediments can act as a source of pollution at sea. Sediments are sinks of hazardous substances, but if the contaminated sediments are disturbed, resuspension of hazardous substances can occur (HELCOM 2010a). Changing oxygen conditions in the bottom of the sea can cause release of metals from the sediment to the water column (Jacobs and Emerson 1982, Brügmann et al. 1997, Ryan 2014, Gubelit et al. 2016).

1.3. Distribution of heavy metals in aqueous environment

The distribution of heavy metals is controlled by many factors. How far a metal travels from the source, depends on its mobility, the hydrographic properties of the water, the water circulation as well as the chemical conditions of the area (Vallius 1999a).

Most heavy metals are easily soluble in oxidizing waters that have low pH, whereas they are precipitated in environments with high pH and low dissolved oxygen. Heavy metals such as Cd, Co, Cu, Pb, Ni and Zn are characterized with this kind of behaviour (Ryan 2014). Between pH 7 – 9 the desorption risk has turned out to be low for most metals, and in acidic waters especially Cu, Zn, As and Cd are released from sediment to the water column (Tzoraki et al. 2017). However, not all elements follow this pattern, Cr and U making an exception (Ryan 2014). The trivalent Cr ion has turned out to be more stable than the hexavalent Cr in natural waters (Lahermo et al. 1996). Hexavalent Cr is most often found in oxidized environments and is the main form in waters with pH above 7, which means that Cr is soluble in alkaline, not acidic, waters. U is also relatively insoluble in acidic waters (Ryan 2014).

Redox reactions affect elements many ways, and they are in an important role while assessing the accumulation of heavy metals in sea bottoms. Often the redox conditions in waters depend on the availability of dissolved oxygen. Redox-dependent elements are present in their oxidized states (Fe^{+3}, Cr^{+6}) in the environments with abundantly dissolved oxygen available (Ryan 2014), and when dissolved oxygen is less available, elements occur in their reduced forms such as S^{-2} in sulfide minerals (Ryan 2014). The redox reactions change the oxidation states of the elements, affecting the solubility of some elements (Ryan 2014). For example, the oxidation state of Cr strongly affects its behaviour in water. Trivalent Cr does not dissolve easily, whereas the hexavalent Cr dissolves in water as oxyanion (Ryan 2014). Another good example is iron: in oxygen-depleted, reducing environments dissolved ferrous iron (Fe^{+2}) is dominant, and in oxidizing environments with abundant oxygen, ferric iron (Fe^{+3}) becomes insoluble (Ryan 2014, Jacobs et al. 1985). Many other heavy metals have various common oxidation states in nature: Mn most commonly occurs as Mn^{+2} and Mn^{+4}, Cu as Cu^{+1} and Cu^{+2}, U as U^{+4} and U^{+6} and As as As^{+3} and As^{+5} (Ryan 2014, Lahermo et al. 1996).

Redox reactions also influence elements that have only one oxidation state in nature: for example, Ni^{+2} is released from iron hydroxide in a reducing environment through iron reduction (Ryan 2014).

Other metals co-precipitating with Mn and Fe hydroxides and oxyhydroxides are Zn, Pb, Cd (Vallius and Leivuori 2003) and Cu (Müller 1999, Vallius and Leivuori 2003).

Eutrophication also plays a role in metal distribution. Increasing growth of algae means more intense decomposition of organic matter in the sea bottom, which consumes oxygen and as a result, the amount of dissolved oxygen in the water decreases and reducing conditions are created (Ryan 2014). At anoxic, oxygen-depleted bottoms with reducing conditions most heavy metals such as Cd, Co, Cu, Pb and Zn are much more likely to occur in the sediment than dissolved in the water column (Jacobs et al. 1985, Borg and Jonsson 1996, Brügmann et al. 1997, Gubelit et al. 2016, Majithiya et al. 2018). Vallius (1999a) suggests that the recent, strong algal blooms and poor oxygen conditions in the near bottom waters in the eastern Gulf of Finland may have increased the accumulation of Cd, Cu and Zn. In addition, the change in redox conditions can cause a release of redox sensitive metals, such as Fe and Mn from sediment to the water column (Jacobs and Emerson 1982, Brügmann et al. 1997, Ryan 2014, Gubelit et al. 2016).

Many elements bond with sulphur and form practically insoluble sulphides (Lahermo et al. 1996). The most common sulphides are iron sulphides, such as pyrite FeS_2 (Ryan 2014). Since many heavy metals have the ionic radii and charge like Fe, the sulphide anion (S^{-2}) forms bonds with several heavy metals, and metals such as As, Cu, Ni, Pb and Zn substitute Fe in pyrite, forming their own heavy metal–sulphide minerals (Ryan 2014). These sulphide minerals crystallize under reducing conditions (Ryan 2014), but if the redox conditions change and anoxic sea bottoms are oxygenized, these minerals become unstable and will dissolve, releasing the metals (Brügmann et al. 1997). Ni does not seem to form sulphides, and in anoxic environments where bonding with sulphur is dominant for most metals, dissolved Ni shows rather unchanged concentrations in the water column (Jacobs and Emerson 1982, Jacobs et al. 1985, Brügmann et al. 1997). Müller (1999) suggested both detrital and Fe hydroxide bonding for Ni.

Organic matter has an influence on the distribution patterns of heavy metals (Müller 1999, Vallius and Leivuori 2003), and high positive correlations between the contents of metals and organic matter have been discovered (Leivuori 1998, Leipe et al. 2013, Gubelit et al. 2016). However, some studies have not been able to establish a correlation between the contents of organic matter and heavy metals (Müller 1999, Vallius and Leivuori 2003). The decomposition of organic matter can cause a change in bonding types of heavy metals (Müller 1999). The decomposition process releases Cu, Cd and Zn when oxic conditions prevail (Vallius and Leivuori 2003), but if sulphur is available, metals can precipitate as sulphides and be trapped in the sediment (Müller 1999). The better preservation of

organic matter in the sites with low oxygen concentrations needs to be considered, when comparing the heavy metal and organic matter contents (Müller 1999).

The release of heavy metals bound with oxides or hydroxides from the sediments to the water column decrease the metal concentration in the sediments (Müller 1999), while the migration of dissolved metals in the pore water toward the sediment surface and their re-adsorption or precipitation at the sediment surface increases the metal concentrations on the sediment surface (Widerlund and Ingri 1995, Müller 1999). Bioturbation can disturb the vertical distribution patterns, while the biota brings the material from lower layers to the sediment surface (Leivuori and Vallius 2004). Borg and Jonsson (1996) found relatively low Hg concentrations at anoxic sites, and suspected that the absence of Hg in the sediments may be caused by the dissolved Hg complexes or Hg methylation which removes Hg from anoxic sediments to oxidized areas.

Grain size also has an influence on the distribution of heavy metals (Ryan 2014). Several studies indicate that the heavy metals are enriched in the finer grain size fraction (Boldrin et al. 1989, Lee and Cundy 2001, Kang et al. 2017, Anbuselvan et al. 2018, Wang et. al 2018), which indicates that that clay minerals have a significant role in the metal distribution (Pye 1994, Ryan 2014). Their small size (< 2 micrometers) typically makes them very reactive, especially because of their relatively high surface area in comparison to the volume (Pye 1994, Ryan 2014), which means that pollutants are more easily absorbed to very fine-grained material than on coarser grains (Pye 1994, Ryan 2014). Also, the small size of clay minerals makes them extremely mobile in the physical sense, and they tend to transport heavy metals as well as other contaminants to distant locations (Ryan 2014). Fine-grained sediments usually have high concentrations of organic matter (Boldrin et al. 1989).

Extremely fine-grained particles of diameter less than 1 micrometer are called colloids (Ryan 2014). Smectite group, Fe and Al hydroxides and humic organic compounds are examples of colloids. Their surfaces are highly reactive exchange sites, which enables the transportation of otherwise immobile elements such as As, Pb and U (Ryan 2014). A process called flocculation is very important on estuaries, where rivers bring material to the sea (Pye 1994). Colloids tend to remain suspended regardless the flow rate and get deposited out of suspension only due to flocculation (Ryan 2014). In order to flocculation to occur, the attractive forces need to overcome the repulsive forces maintained by the similar electrical double layer on clay minerals' surfaces (Pye 1994, Poleto and Charlesworth 2010). Flocculation is facilitated in saline water (Poleto and Charlesworth 2010), where electrolytes make the layer of ions surrounding the clay minerals thinner, and the particles can get closer to each other and the positively charged edges of some clay particles are attracted to the negatively charged

surfaces of other particles (Pye 1994). Jilbert et al. (2018) studied the estuarine sediments in the western Finland coast of the Gulf of Finland and discovered that flocculation alters dissolved organic matter and Fe into their particulate phases, but the process is partially decoupled due to the different response to estuarine mixing shown by Fe associated with dissolved organic matter compared to colloidal Fe. The zone of the Fe flocculation in the water column occurs in the proximity of the first contact between the fresh water and more saline water, in rather low salinities, and causes the accumulation of dissolved Fe and Fe associated with organic matter to occur near the shore (Jilbert et al. 2018). The distribution of flocculated Fe was also affected by the bathymetry – probably related to shelf-to-basin transfer (redox shuttling) and transport by currents that take fine-grained material to the deeper parts (Jilbert et al. 2018).

1.4. Sediment quality guidelines and background values

Knowing the concentration of metals in sediments is more useful, if the toxicity to the benthic organisms is considered (Vallius 2015a, 2015b). Sediment quality guidelines (SQGs) are useful tools in assessing the concentrations of harmful substances and the adverse effects in marine biota when exposed to those substances (CCME 2001). Since local SQGs are not available for the Gulf of Finland, metal concentrations have been compared to the criteria developed in another areas in order to get a better understanding of the degree of contamination in the Gulf of Finland.

The classification by Vallius and Leivuori (2003) is based on the Swedish marine sediment quality criteria. Vallius and Leivuori (2003) chose the Swedish values, because the earlier measurements by Vallius and Leivuori (1999) in the Gulf of Finland from the depth of 25 cm may have set the background values too high due to the shallow sampling depth, especially in the case of Cu and Zn. Estimated background values for the Gulf of Finland by Vallius and Leivuori (1999) were Pb 21, Hg 0.018, Cu 25, Cd 0.11 and Zn 100 mg/kg. The Swedish values were measured at a depth of about 55 cm and are believed to represent pre-historial times (Swedish Environmental Protection Agency 2000). However, the sedimentation rates especially at coastal areas can be almost 2 cm/year (Kankaanpää et. al 1997) – with such a high accumulation rate this sediment depth of 55 cm would represent only a few decades. The Swedish criteria have five classes – the boundary between classes 1 and 2 is represented by the reference/background value, classes 2, 3 and 4 represent an increasing amount of diffuse pollution sources, and the class 5 indicates local source pollution (Swedish Environmental Protection Agency 2000). Vallius et al. (2007) compared their results from north-eastern Gulf of Finland with the classification of Vallius and Leivuori (2003), and states that the use

of the classification based on the Swedish criteria in the Gulf of Finland is problematic due to too narrow ranges between the classes and geological differences. The chemical composition of the soft sediments on the Vyborg rapakivi massif and areas dominated by supracrustal rocks are significantly different (Vallius et al. 2007), and therefore knowing the local background concentrations is crucial in defining the toxicity levels of sediments. Vallius (2007) presented background concentrations for selected metals and compared them with the Swedish criteria. The background values by Vallius (2007) differ from the Swedish values (Table 1). This is probably due to geological differences, but since the criteria used for the Swedish guideline values is not known, the real reason for this remains a mystery (Vallius 2007).

	Swedish background values (mg/kg)	**Background values (mg/kg) by Vallius (2007)**
As	10,0	16,4
Cd	0,20	0,16
Co	14,0	15,6
Cr	80,0	69,4
Cu	15,0	30,2
Ni	33,0	34,9
Pb	31,0	24,0
Hg	0,040	0,017
Zn	85	120

Table 1. Comparison between the Swedish values from samples taken at a sediment depth of about 55 cm (mg/kg dry weight, Swedish Environmental Protection Agency 2000) and the background values for eastern Gulf of Finland presented by Vallius (2007, varying depths: estimated minimum ages of 80 – 100 years). The values are median values.

To understand the toxicity levels in the Baltic Sea and especially the Gulf of Finland sediments, Vallius (2014, 2015a, 2015b) compared the heavy metal concentrations in the Baltic Sea sediments to the sediment quality guidelines from North America. Vallius (2015a) compared the metal concentrations of off-shore sediments in the Gulf of Finland to both the United States SQGs by Long et al. (1995) and the Canadian SQGs by the Canadian Council of Ministers of the Environment CCME (2002), and came to the conclusion that the Canadian SQGs are better suitable as guidelines for the Gulf of Finland than the older, US guidelines. In some cases, the lower reference values are probably too low for the Gulf of Finland, but in general, the Canadian SQGs seem to be valid and realistic for studied elements (As, Cd, Zn, Cr, Hg, Pb, Cu), and could be used in defining the toxicity levels of

sediments in the Gulf of Finland (Vallius 2015a, 2015b). Vallius (2015a) states that even though the results need to be interpreted with caution, it is better to have guidelines made for another area than to have nothing to compare with.

There are two reference values in the Canadian SQGs (CCME 2002); the lower reference value called the interim sediment quality guideline (ISQG) and the higher reference value called probable effect level (PEL). The ISQG value can be considered as a threshold effect level (CCME 2002). Below the threshold effect level concentration adverse biological effects occur infrequently, whereas above the PEL level these adverse effects occur frequently (CCME 2001). In the US SQGs the values are called Effects Range-Low (ERL) and an Effects Range-Median (ERM), and they define concentration ranges that are associated with adverse biological effects rarely, occasionally or frequently (Long et al. 1995). The Canadian and the US guideline values for As, Cd, Cr, Cu, Pb, Hg and Zn are presented in Table 2.

	ISQC	**ERL**	**PEL**	**ERM**
As	7,24	8,2	41,6	70
Cd	0,7	1,2	4,2	9,6
Cr	52,3	81	160	370
Cu	18,7	34	108	270
Pb	30,2	46,7	112	218
Hg	0,13	0,15	0,70	0,71
Zn	124	150	271	410

Table 2. The Canadian guideline values ISQC and PEL (CCME 2002) compared with the US values ERL and ERM (Long et al. 1995) for seven metals. The values are presented in mg/kg.

1.5. Distribution of heavy metals in Gulf of Finland

The distribution patterns of heavy metals can be compared horizontally or vertically. The horizontal comparison shows the regional difference in their distribution, whereas vertical comparison reveals the pollution history (Vallius 1999a). Even though the concentrations of heavy metals have decreased during last decades in the Gulf of Finland (Vallius 1999a, 1999b, 2014, Leipe et al. 2013), the pollution problem still exists since the concentrations of some elements, such as Cd, Zn and Co, are still too high (Vallius et al. 2007, Vallius 2015a). In the eastern and north-eastern parts of the Gulf, also Hg shows rather high concentrations (HELCOM 2010a).

The concentrations of most heavy metals (Cd, Zn, Cu, Hg, Pb) and As reach their highest levels in the eastern and north-eastern parts of the Gulf of Finland (Leivuori 1998, Vallius and Leivuori 2003, Leivuori and Vallius 2004, HELCOM 2010a, Vallius 2015a, 2015b). The most contaminated areas in the Gulf of Finland seem to be the mouth of River Kymi, the Neva Estuary and the Bay of Viborg (Leivuori 1998, Vallius 1999a.) The Kotka-Hamina sea area in the outlet of River Kymi is an especially badly polluted area, and it may even be the worst polluted area in the entire Baltic Sea (Vallius et. al 2007). Especially Hg and Cd have high concentrations in the surface sediments in this part of the Gulf (Leivuori 1998, Vallius et al. 2007, HELCOM 2010a). The contamination of Hg from River Kymi has ceased decades ago, but Hg still affects the environment through resuspension and seaward transportation (Vallius 2015b). Also, the concentrations of Co and Zn are still too high in the surface sediments (Vallius et al. 2007), even though the vertical comparison shows that concentrations of most metals have had a decreasing trend during the last decades (Vallius et al. 2007, Vallius 2015b). Cd and some other metals, such as Co and Zn, are assumed to be transported towards west from the easternmost parts of Gulf of Finland (Vallius et al. 2007). Leivuori (1998) discovered that the mean concentration of Cr is highest in the eastern parts of the Gulf of Finland, in the sediments of Vyborg Bay and the Neva estuary, but in the more recent study by Vallius (2015b) no significant differences in the concentrations of Cr between the eastern and western parts of Gulf of Finland are observed, the concentrations being only slightly higher in the east. Even though the As concentrations in the eastern parts of the Gulf appear to be slightly higher than in the west, the concentrations are not remarkably higher, and the concentrations are relatively low and close to the estimated background values – the concentrations vary between 14 – 16 mg/kg in the sediments of the Gulf (Leivuori and Vallius 2004). According to the study of Gubelit et. al (2016), the levels of Mo, Ni and Co in the water column are elevated in proximity of the Leningrad Nuclear Power Plant in the Neva

estuary, and Pb, Co, and Zn are the main pollutants in both water column and sediments in the eastern Gulf of Finland.

According to Vallius (2015b), only the concentrations of As, Cd, Hg and Zn exceeded the PEL levels in the sediments near the northern coast of Gulf of Finland. From the surface until the depth of 20 centimetres, the levels were exceeded by As, Cd and Zn, which means that only those metals are a threat to benthic species since only a few organisms burrow deeper than 20 centimetres in the sea bottom. However, strong currents or human activity may cause the release of older sediments to the water column (Vallius 2015b). The higher As concentrations in the surface sediments compared to the deeper ones may be explained by the adsorption of Fe in the oxic sediments layers (Widerlund and Ingri 1995, Vallius 2014).

2. STUDY GOALS

The goals of this study are (1) to establish the horizontal distribution of heavy metals in the surface sediments of north eastern Gulf of Finland, (2) reveal changes in the heavy metal deposition of the study area over time, (3) establish the correlation between the deposited heavy metals and organic matter in the surface sediments, (4) to determine the causes for the observed distributions, and (5) to determine the degree of contamination of the study area.

3. DESCRIPTION OF THE STUDY AREA

3.1. The study area

The study area is situated in the municipalities of Kymenlaakso and eastern Uusimaa in the Eastern Gulf of Finland (Figure 2). In Kymenlaakso, the surface sediment samples of the study were collected near the coast in Klamila, Ravijoenlahti, Kotka, Hamina and Parlahti. The locations in the archipelago were located in Mustamaa, Ulko-Tammio, Itäsyvä, Kauholma, Rakin-Kotka, Majasaari, Suuri-Musta and Ristisaari. One sampling site, Luodematalat, was located offshore. The core sampling sites are near Ravijoki, Rakin Kotka and Kuorsalo (Figure 2). In the western part of the study area, the samples were collected near the coast in Svartholmen east of Loviisa, in Skatahället, Sarvisalo and Pellinki between Loviisa and Porvoo and in Varpudden, a site west of Porvoo.

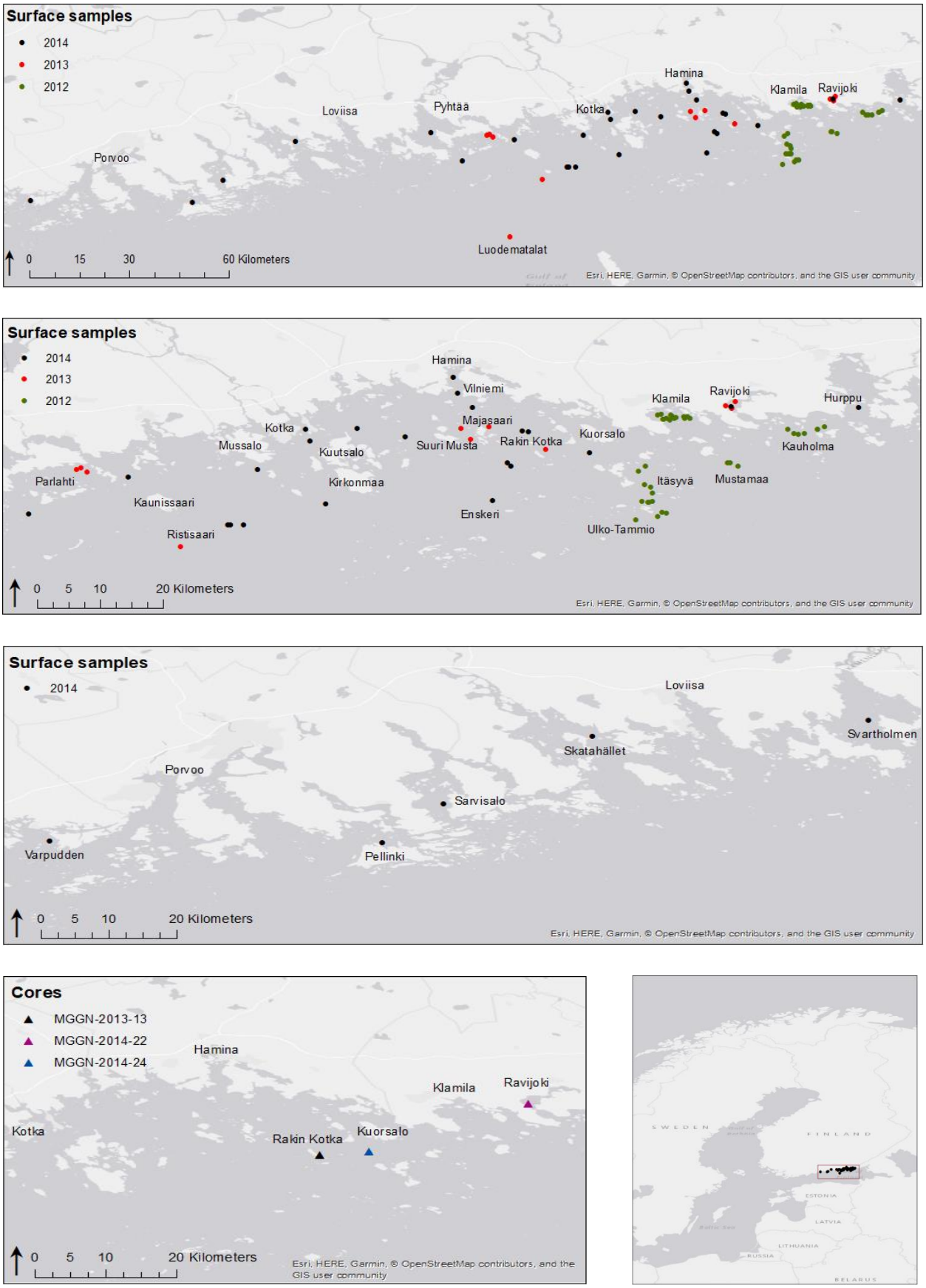

Figure 2. The samples were collected from the north-eastern Gulf of Finland. The uppermost picture shows the sampling sites for all surface samples, and the pictures in the middle a closer look at the location of the sites in the eastern and western parts of the study area.

3.2. Bedrock and seabed substrates

The bedrock on the study area consists mainly on viborgite, a type of rapakivi granite. When rapakivi granites are compared to the chemical composition of granites, higher average concentrations of Si, K, F, Rb, Ga, Zr, Hf, Th, U, Zn and REE's are observed in rapakivi granites, but in contrast, the concentrations of Ca, Mg, Al, P and Sr are lower (Rämö et al. 1998).

Sedimentation basins in the north-eastern parts of the Gulf of Finland are mainly larger than in other parts of the Finnish coast: on this part of the Gulf, the islands are more scarcely situated and are generally larger, which makes the open sea area between the islands wider (Vallius 2011). On the northern coast of the Gulf, where the bedrock has partially eroded and gone through faulting and glacial scouring (Kaskela and Kotilainen 2017), the fragmentation can be seen in the underwater landscape, too, as elevations and depressions (Kaskela et al. 2016). The areas with the highest geodiversity are found on crystalline bedrock, whereas more homogenous areas are located on the sedimentary rocks (Kaskela and Kotilainen 2017). The seafloor of the Gulf of Finland, and especially the northern coast, is highly heterogenous with diverse geomorphological features, such as plains, valleys, basins and elevations (Kaskela et al. 2012, Kaskela and Kotilainen 2017). This geomorphologically variable environment causes the patchy sediment distribution of the study area (Kaskela et al. 2016, Figure 3). The sediments on the seafloor of the study area consist mainly of clay and muddy sand, with some sandy and coarse-grained areas. The seafloor appears to consist of sand and coarse substrate more often in the western parts of the area. Areas of mixed sediment are found throughout the area, and the bedrock is occasionally exposed. Most of the sediments have deposited during or after the latest glaciation (Kaskela et al. 2016).

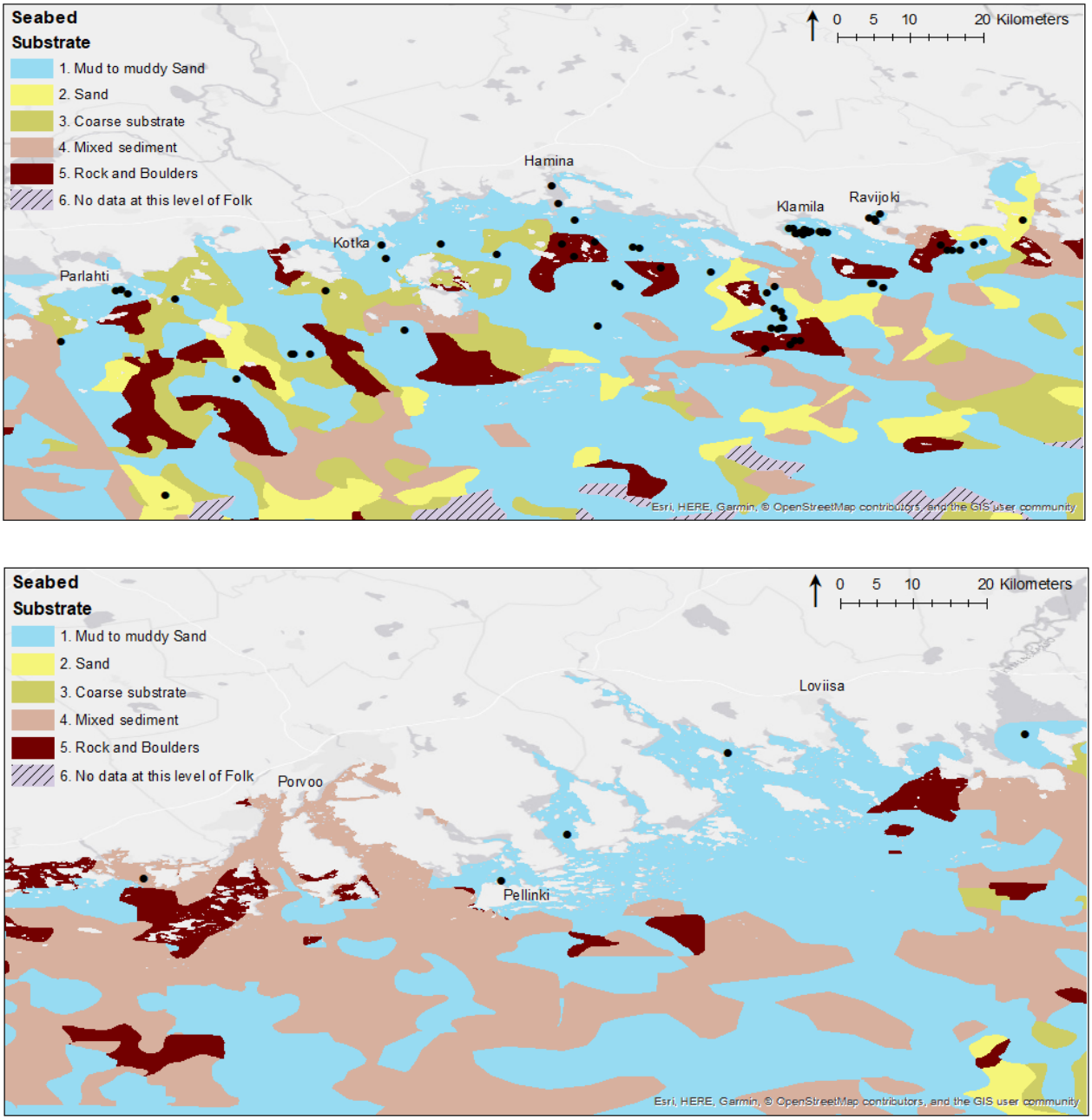

Figure 3. Map of seabed substrates with the sampling sites (GTK). The upper picture presents the eastern part of the study area, and lower one the western part of the area. The sediment distribution is patchy with highly heterogenous sediments within a small area, especially in the eastern part of the study area.

4. MATERIAL AND METHODS

4.1. Sample collection

Samples were collected by GTK staff during TOPCONS sampling cruises in 2012 and 2013, and during the RAUSKU cruise in 2014 (Kotilainen et al. 2012, Kaskela et al. 2013, Kotilainen et al. 2014). The sampling sites were chosen based on acoustic-seismic survey data, which was collected earlier (Kotilainen et al. 2012, Kaskela et al. 2013). During the 2012 cruise, samples were collected from Klamila, Mustamaa, Kauholma, Itäsyvä and Ulko-Tammio during 1. – 6.10.2012 with the research vessel Geomari (Figure 2, Kotilainen et al. 2012). In the following year, samples were collected during 9. – 20.9.2013 with Geomari from the sampling sites located in Parlahti, Ristisaari, Luodematalat, Rakin Kotka, Majasaari, Ravijoenlahti and Suuri-Musta (Figure 2, Kaskela et al. 2013). In 2014, the sampling sites were located in Varpudden, Pellinki, Sarvisalo, Skatahället, Svartholmen, Kaunissaari, Enskeri, Mussalo, Kotka, Kirkonmaa, Vilniemi, Rakin Kotka, Kuorsalo, Ravijoenlahti and Hurppu (Figure 2). The samples were collected during 12. – 26.9.2014 with Geomari (Kotilainen et al. 2014).

On the TOPCONS and RAUSKU cruises, the same equipment was used. The surface sediments from soft bottoms were collected with a GEMAX twin barrel gravity corer (inner diameter was 9 cm of the core liner) and a box corer. GEMAX had an inner diameter of 90 mm of the core liner and the box corer's inner box was 184 mm wide, 183 mm long and 255 mm high. Photographing and documentation of the sediment cores were done onboard during all cruises using standard GTK description forms. Sedimentological descriptions of GEMAX core were performed both through the plastic core liner, and from the trimmed and split sediment surfaces. The descriptions of the box cores were also made both through the plastic core liner and after the removal of the plastic box, from the trimmed sediment surfaces. All the sediment cores were then subsampled onboard, and then kept in cold. The sediment cores taken by GEMAX and the box corer were sliced, and the subsamples were packed in plastic bags and boxes (Kotilainen et al. 2012, Kaskela et al. 2013, Kotilainen et al. 2014).

4.2. Textural, geochemical and statistical analyses

The textural analysis was done by GTK staff taking part in the expeditions. Preliminary observations onboard discovered geological differences between the study areas on cruise in 2012. The sediments at Klamila seemed relatively homogenous and they were mostly silt and clay, whereas the Kauholma sediments revealed sand at the seafloor. The sediments at Mustamaa were more heterogenous (Kotilainen et al. 2012). Differences between study areas were discovered also onboard in 2013. Parlahti sediments showed modern mud and it was defined as an accumulation area, Ristisaari was revealed as an underwater continuation of an esker with an occasionally anoxic muddy basin in the west, Luodematalat sediments were sandy, Rakin Kotka sediments were mainly modern mud that thinly covered sand and coarse sediments and many sites showed anoxia, Majasaari sediments were modern mud and sand with some anoxic sites, Ravijoenlahti mostly bioturbated mud, and Suuri-Musta sediments were sand and gravel (Kaskela et al. 2013).

The surface of the core MGGN-2013-13 had a black colour, and bubbles of gas were observed. The inspection of the split core showed that the sediment was laminated sulphide mud from the surface until the depth of 35 cm. The laminae were black, grey and dark grey, each 1 – 3 cm thick. From 35 cm to 45 cm, the sediment was homogenous grey mud. A sulphide layer at sediment depth of 36,5 cm to 37 cm was observed. The water depth at the sampling site was approximately 22 metres.

The surface of the core MGGN-2014-22 was oxidized fluffy brown mud and had worm burrows. The inspection of the split core revealed that the thickness of the oxidized surface layer was 4 cm. At the depth of 4 – 9 cm, the mud was brownish-grey and sulphide-mottled with gradational upper contact. The sediment then turned into greyish brown coloured, bioturbated (Marenzelleria viridis) mud with sulphide-mottling in the upper part. From 24 – 37 cm, the sediment was weakly laminated dark grey mud with gradational upper contact. Then the sediment gradually changed into brownish grey mud with homogenous texture (37-51cm). The water depth at the sampling site was 3,5 metres.

The surface of core MGGN-2014-24 was black fluffy mud. From the sediment surface until the depth of 31 cm, the laminae were visible in the mud. The laminae were dark grey with thickness of 1 – 4 mm, black with thickness of 3 – 20 mm and light olive grey with thickness of 1 – 4 mm. There was a 2 cm thick black layer at sediment depth of 10 – 12 cm. Laminae counting resulted in 40 – 45 triplets. At sediment depth of 31 cm, the sediment began to gradually change into bioturbated brownish grey mud (31 – 40 cm). From 40 cm to 46 cm, the sediment was blackish grey mud with undulating upper contact and homogenous texture. From 46 to 50 cm, the mud was weakly laminated, partly

bioturbated and sulphide mottled, with relatively sharp upper contact. The water depth at the sampling site was 22 metres.

The chemical analysis was performed at Labtium. The samples were digested in hydrofluoric-perchloric acid to release the elements from the solid soil phase. Elemental compositions were determined using inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma–optical emission spectrometry (ICP-OES), CHN-analyser and a pyrolytic determination method for Hg. The Cs concentration was determined with a multichannel analyser ORTEC ACE 2K the GTK.

In the ICP-OES technique, the concentration of an element is determined by the intensity of the light emitted at the typical wavelength for that element, whereas in the ICP-MS technique the elements are determined by using a mass spectrometer based on the elements' mass-to-charge ratio (Laing 2010). The Hg pyrolysis technique is based on heat: the Hg compounds decompose while heated (Biester and Nehrke 1997). In the combustion analysis, the samples are combusted at high temperatures (>1000 °C) by the CHN analyser, which then identifies the combustion products (Kristensen and Andersen 1987).

The elements for the chemical analysis were chosen by GTK staff. To analyse the surface samples collected in 2014 and all the core samples, the ICP-MS technique was used to determine the concentrations of Ce, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nd, Pr, Sm, Ta, Tb, Th, Tm, U, Yb, As, Bi, Cd, Mo, Pb, Sb, Sn, and Tl, and the ICP-OES technique was used to determine Al, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Rb, S, Sc, Sr, Ti, V, Y and Zn. Instead of using ICP-OES, the ICP-MS technique was used to determine Be, Co, Cr, Cu, Ni, Rb, V, Sc and Y in the surface samples collected in 2012 and 2013. A combustion analyser was used to determine C and N, and pyrolytic determination was used to measure Hg in both core and all the surface samples.

After analysing the concentration vs. sediment depth diagrams of 41 elements, 17 elements were chosen for this study. The decision was made based on the concentration changes the metals showed over time, but also the changes observed between the three cores. The elements of the lanthanide group showed highly similar behaviour in the diagrams, thus La was chosen to represent the lanthanide group elements.

The Cs concentrations measured in the core MGGN-2013-13 was compared to the chosen elements from the same core, to estimate the deposition of the elements over time. The concentrations from all three cores, MGGN-2013-13, MGGN-2014-22 and MGGN-2014-24 were compared to establish

regional changes in the pollution history of each element. Horizontal distribution maps from surface sediment data were produced to estimate the areas of most intense deposition of the studied elements.

Pearson correlation coefficient (r) was calculated between chosen elements, sand, silt, clay and C to establish the correlations. The grain size distribution data was available only for the sediment samples collected in 2012.

Both the core and surface samples were compared to the background levels and the Canadian SQGs in order to estimate the degree of the contamination of the study area.

5. RESULTS

5.1. Vertical distribution

5.1.1. Metal concentrations over time in the core MGGN-2013-13

In the core MGGN-2013-13, the peak of Cs concentration appears at sediment depth of 19 – 20 centimetres (Figure 4). In the Baltic Sea sediments, this concentration peak represents the Chernobyl nuclear power plant accident in 1986. The comparison between the Cs and metal concentrations enables to estimate the change of metal concentrations at given location over time. In general, the metal concentrations have declined since 1986 (Figures 4 and 5).

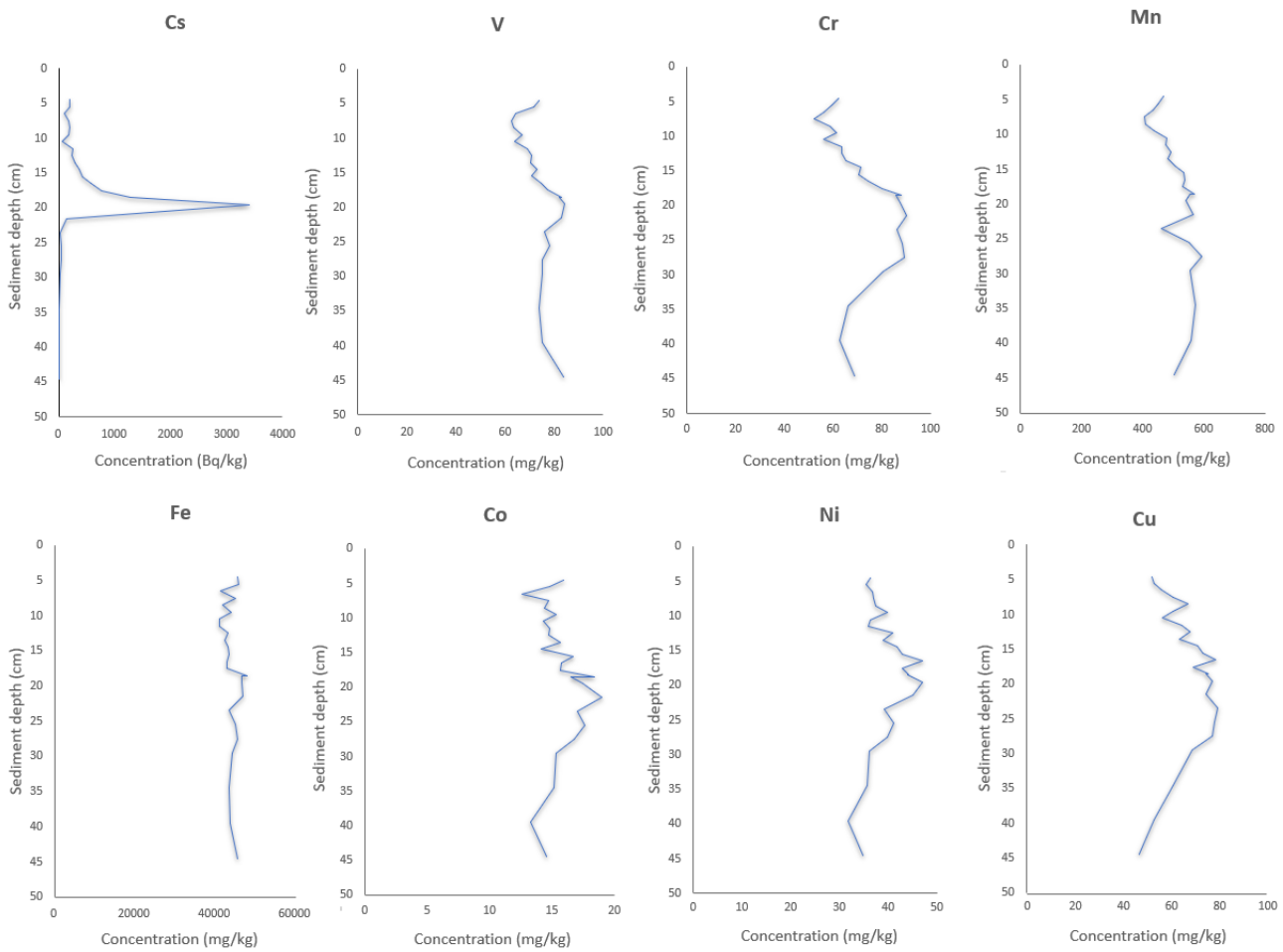

Figure 4. The concentrations of radionuclide Cs and transition metals V, Cr, Mn, Fe, Co, Ni and Cu in the core MGGN-2013-13.

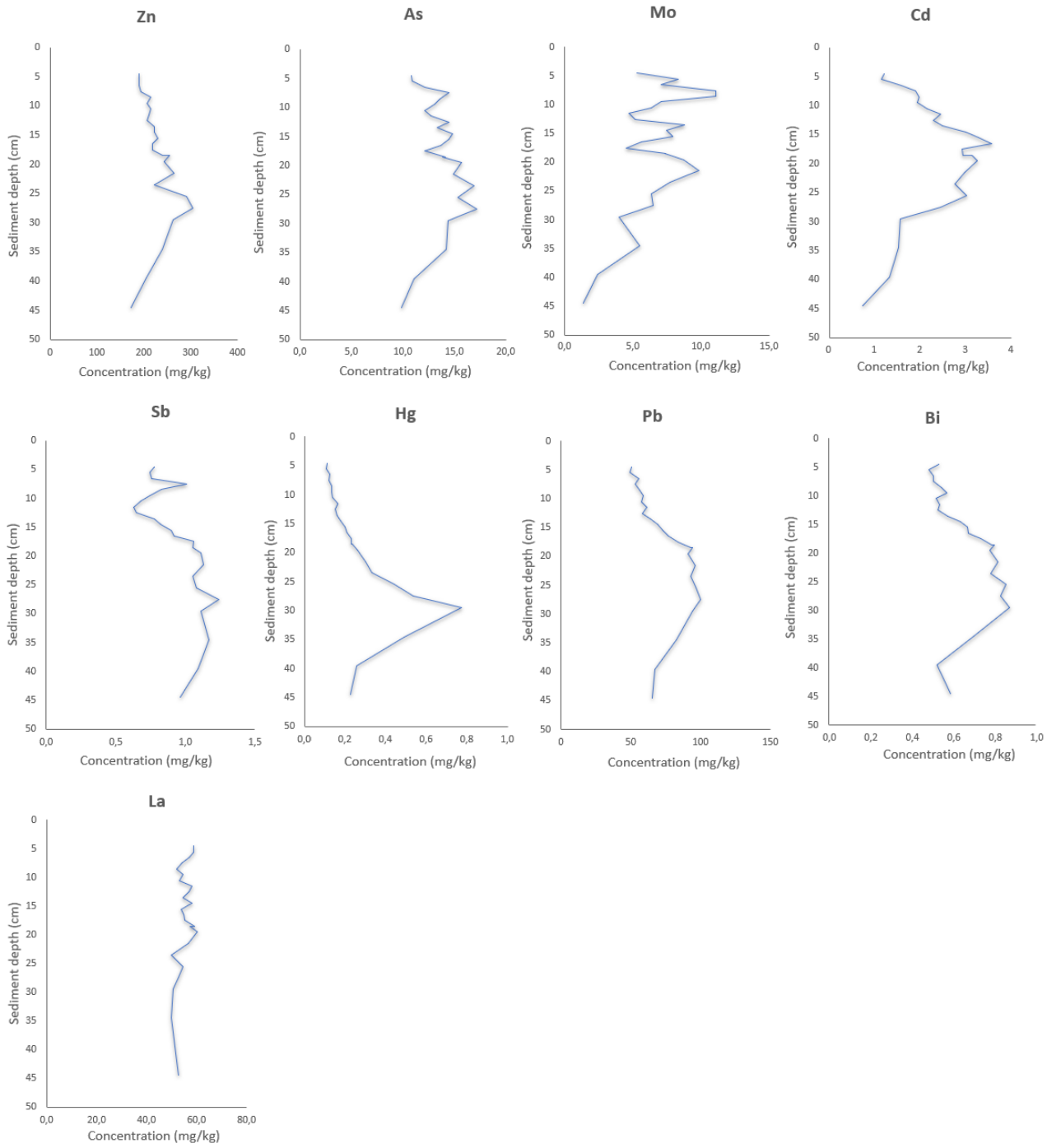

Figure 5. The concentrations of transition metals Zn, Mo, Cd and Hg, metalloids As and Sb, post-transition metals Pb and Bi, and La in the core MGGN-2013-13.

Most transition metals have a similar, general trend in the core MGGN-2013-13. The metal concentrations in the core MGGN-2013-13 showed often a steady increase, followed by periods of maximal deposition, after which point the concentrations began to decline (Figures 4 and 5). However, the inclining and declining rates and times for maximal deposition varied among studied

transition metals. Some metals (V, Cr, Fe, Co, Ni) showed initial decline in the deepest sediments at the bottom of the core. For certain transition metals (V, Cr, Mn, Co, Cd, Mo), the concentrations appear to increase towards the recent sediments. The maximal deposition occurred around mid-1980's for V, Fe and Ni, whereas the maximal deposition of others (Cr, Co, Cu, Hg, Zn) occurred before that. In contrast, the highest concentrations of Mo and Cd were measured after the mid-1980's. Hf and Mo showed different concentration pattern compared to other transitions metals. The concentrations of Hf have not changed significantly over time, whereas Mo concentrations showed stronger changes and rapid decline towards the recent sediments.

The highest concentrations of both studied metalloids, As and Sb, occurred before the mid-1980's (Figure 5). Sb declined steadily since mid-1980's until the sediment depth of 12 centimetres, after which point the concentrations began to increase, followed by a relatively rapid decline. In the most recent sediments, the concentrations appear to increase again. The As concentrations appear to follow the same concentration pattern as most transition metals. The concentrations increase at first reaching the maximal deposition, after which the trend seems to be declining.

The concentration patterns of post-transition metals Pb and Bi showed similarities with the concentrations of transition metals. The concentrations increased steadily until the peak concentrations, after which point the concentrations began to decline (Figure 5). The maximum concentrations of Pb and Bi occurred before the mid-1980's and have declined ever since. However, the concentrations of both metals appear to increase towards the most recent sediments.

The concentrations of La have not changed significantly over time (Figure 5). The highest concentrations for La are measured around mid-1980's or right after that, at sediment depth of around 19-20 centimetres. After this point, the concentrations remained at slightly higher levels than the initial concentration measured at the depth of 45 centimetres.

5.1.2. Metal concentrations over time

For V, the concentration pattern of the core MGGN-2014-22 differs from the cores MGGN-2013-13 and MGGN-2014-24 (Figure 6). The V concentrations in the core MGGN-2014-22 increase over time, and the concentration of 67 mg/kg measured at the most recent sediment is higher than the concentration of 54 mg/kg measured at the bottom of the core at depth 58,5 cm. The V concentrations in cores MGGN-2013-13 and MGGN-2014-24 have a declining trend since the time of maximal

deposition, and the concentrations measured at the most recent sediments are lower than the concentrations measured at the bottom of the core.

The Cr concentration changes at core MGGN-2014-22 are more modest than at other two cores (Figure 6). The peak concentration of 68,6 mg/kg at sediment depth of 13,5 cm at core MGGN-2014-22 is lower than the peak concentrations at cores MGGN-2013-13 (90,2 mg/kg at sediment depth of 21,5 cm) and MGGN-2014-24 (94,8 mg/kg at 9,5 cm). The concentration trends are clearer at cores MGGN-2013-13 and MGGN-2014-22 than at core MGGN-2014-24, where the concentration changes are relatively rapid. The Cr concentrations at core MGGN-2014-22 have remained at only a slightly lower level than the maximal deposition levels until the most recent sediments, whereas the concentrations at cores MGGN-2013-13 and MGGN-2014-24 have significantly declined, when the peak values and the concentrations in the most recent sediments are compared.

The Mn concentration curves of cores MGGN-2013-13 and MGGN-2014-14 resemble each other, whereas the curve of core MGGN-2014-22 differs from other two cores, and the concentration changes are more moderate (Figure 6). The concentrations towards the most recent sediments appear to increase at cores MGGN-2014-22 and MGGN-2013-13, whereas the trend is opposite at MGGN-2014-24.

The Fe concentrations remained between certain levels at cores MGGN-2013-13 and MGGN-2014-24 and have not changed significantly over years (Figure 6). The concentrations at core MGGN-2014-24 decreased rapidly towards the most recent sediments, and the latest concentration (32 900 mg/kg at 0,5 cm) is lower than the value measured from the bottom of the core (38 000 mg/kg at 70 cm). The concentrations at core MGGN-2014-22, however, have increased steadily towards the most recent sediments, and the concentration measured at 0,5 cm (48 700 mg/kg) is higher than the one measured at the bottom of the core at depth of 58,5 cm (37 300 mg/kg).

The concentration curves of Co are similar in all three cores until the maximal deposition. The Co concentrations first decreased, and then began to increase (Figure 6). After reaching their peak concentrations (16,8 mg/kg at 19,5 cm for core MGGN-2014-24 and 19 mg/kg at 21,5 cm for core MGGN-2013-13), the Co concentrations began to decrease at cores MGGN-2013-13 and MGGN-2014-24. Even though the concentrations increased at some points, since the peak value, the general trend is decreasing for both cores. However, after the peak value, the concentrations at core MGGN-2014-24 remained at relatively high level between 17,1 mg/kg and 20,8 mg/kg, which is higher than

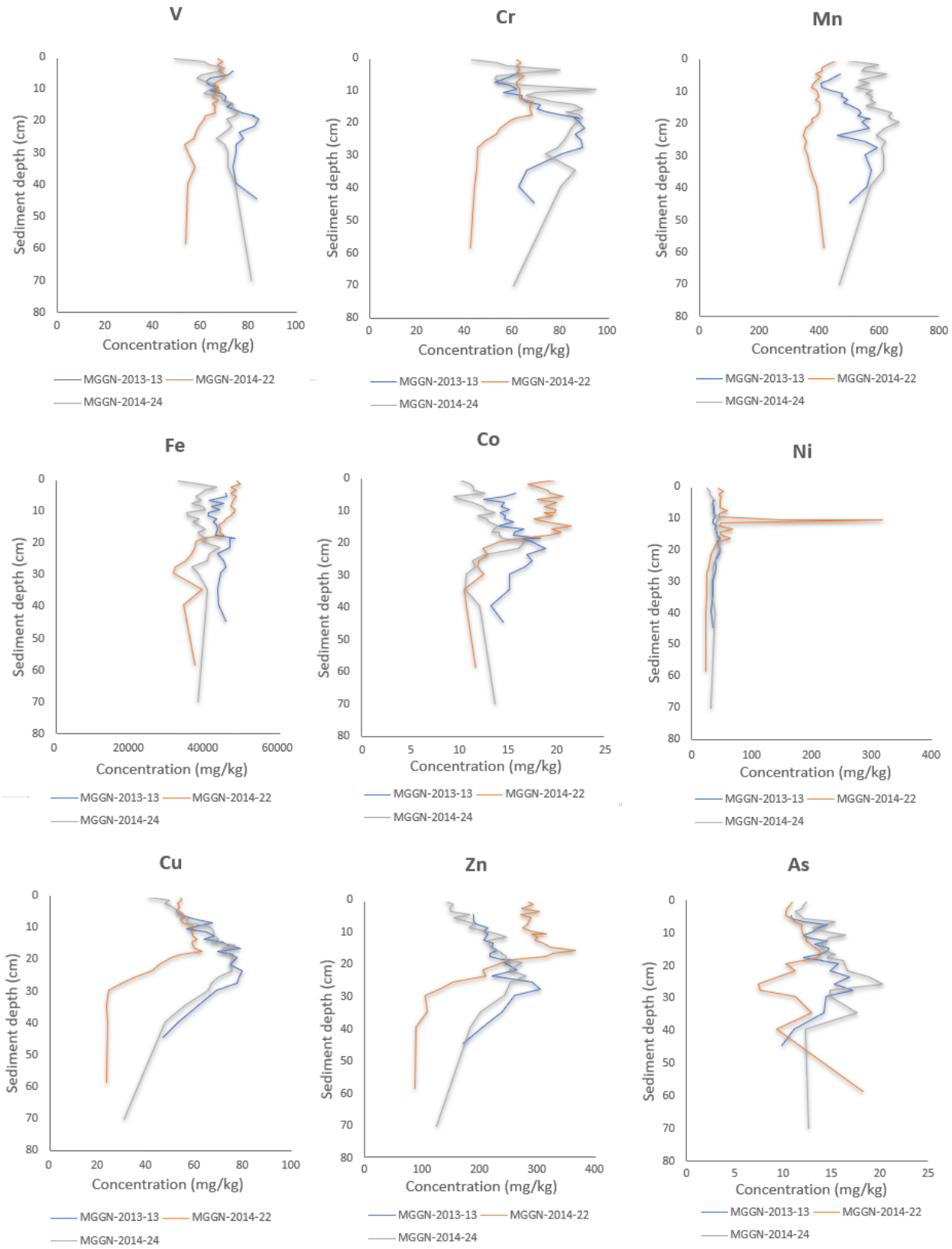

Figure 6. The concentrations of V, Cr, Mn, Fe, Co, Ni, Cu, Zn and As in the cores MGGN-2013-13, MGGN-2014-22 and MGGN-2014-24.

the initial value of 11,8 mg/kg. In the core MGGN-2014-22, the Co concentrations have remained relatively high since the maximal deposition.

In the case of Ni, the concentrations remained relatively stable at cores MGGN-2013-13 and MGGN-2014-24 (Figure 6). The concentrations increased slightly at core MGGN-2014-22 at depth of 18,5 – 16,5 cm from 44,5 cm/kg – 64,5 cm/kg, after which point the concentrations decrease and increase repeatedly. The Ni concentration increased rapidly until its peak value of 318 mg/kg at sediment depth of 10,5 cm at core MGGN-2014-22, and then rapidly decreased again.

The Cu concentration curves at cores MGGN-2013-13 and MGGN-2014-24 resemble each other (Figure 6). The concentrations increased until they reached the peak concentrations, which is 79,6 mg/kg at 23,5 cm for core MGGN-2013-13 and 76,5 mg/kg at 15,5 cm for core MGGN-2014-24. After this point, the concentrations began to decrease, and the concentrations in the most recent sediments are close to the initial values. The Cu concentrations of the core MGGN-2014-22 remained stable until 29,5 cm, after which point the concentration began to increase reaching its peak concentration of 62,9 mg/kg at 17,5 cm. After the peak, the concentration began to decline gradually, remaining, however, significantly higher than the initial concentration at the bottom of the core.

The Zn concentration curves at cores MGGN-2013-13 and MGGN-2014-24 resemble each other (Figure 6). From the bottom of the core, the concentrations increase at first, but after reaching their peak values of 305 mg/kg at 27,5 cm for core MGGN-2013-13 and 281 mg/kg at 23,5 cm for core MGGN-2014-24, the concentrations began to decline. The concentration in the most recent sediment at depth of 0,5 cm (141 mg/kg) is higher than the concentration of 125 mg/kg measured at 70 cm for the core MGGN-2014-24, and at core MGGN-2013-13, the concentration of the sediment at depth of 4,5 cm was 182 mg/kg, which is slightly higher than the value measured at depth of 44,5 cm (172 mg/kg). The Zn concentration at core MGGN-2014-22, too, increased until it reached its peak value of 367 mg/kg at sediment depth of 15,5 cm, which is higher than at other two cores and occurred later. Since the peak, the concentrations began to decline at core MGGN-2014-22, but the concentration measured from the most recent sediment (285 mg/kg) is significantly higher than the concentration measured at sediment depth of 58,5 cm (88,5 mg/kg).

The As concentration curves at cores MGGN-2013-13 and MGGN-2014-24 resemble each other, whereas the core MGGN-2014-22 shows a different pattern at some points (Figure 6). After reaching the peak concentrations, 20,3 mg/kg at sediment depth of 25,5 cm for the core MGGN-2014-24 and 17,2 mg/kg at 27,5 cm for the core MGGN-2013-13, the concentrations in both cores MGGN-2013-

13 and MGGN-2014-24 have a declining trend. In case of the core MGGN-2014-22, the lowest concentrations are measured while the other two cores showed the highest As concentrations. After this, the As concentrations in the core MGGN-2014-22 increased and reached the levels of other two cores, and since that the As concentrations at all three cores decreased. However, the concentrations appear to increase towards the most recent sediments at cores MGGN-2014-22 and MGGN-2014-24.

The concentration curve of Mo in the core MGGN-2014-22 differs from the concentration curves of the two other cores (Figure 7). In MGGN-2014-22, the Mo concentrations increased at some points, but are less in the most recent sediments (0,9 mg/kg at 0,5 cm) compared to the initial value of 2,24 cm/kg at 58,5 cm. In the cores MGGN-2013-13 and MGGN-2014-24 the concentration changes are greater than at core MGGN-2014-22. In these two cores, the concentrations increased and decreased at many points, but the general trend appears to be increasing at first. However, the concentrations appear to decrease towards the most recent sediments.

The comparison of the Cd concentrations between all the three cores showed similarities in the Cd trends (Figure 7). The following trend can be seen at all three cores: at first, a modest increase of concentrations, which was followed by a more rapid increase. After that, the concentrations remained between certain levels, and this period was followed by a decline. These changes first appeared at core MGGN-2013-13, followed by core MGGN-2014-24, and then core MGGN-2014-22. The peak concentrations are measured at sediment depth of 16,5 cm at core MGGN-2013-13 (3,6 mg/kg), at depth of 15,5 cm at core MGGN-2014-24 (3,74 mg/kg), and at depth of 14,5 cm at core MGGN-2014-22 (2,47 mg/kg). In general, the concentration changes at core MGGN-2014-22 are not as strong as at other two cores, and the peak Cd concentration is significantly lower than at other cores. On the other hand, the Cd concentration in the recent sediments appears to be much higher at core MGGN-2014-22 compared to the concentrations of other two cores.

The Sb concentrations remained at lower levels at core MGGN-2014-22 than at cores MGGN-2013-13 and MGGN-2014-24, and the concentration changes are not as great as at other two cores (Figure 7). At MGGN-2014-22, the concentration increased only slightly at first, followed by more rapid increase in concentrations. After reaching the peak concentration of 0,561 mg/kg at sediment depth of 17,5 cm, and after that, Sb concentrations began to decline. The Sb concentration patterns in cores MGGN-2013-13 and MGGN-2014-24 are similar, except for more intense concentration decline in the core MGGN-2013-13 between 20 – 10 centimetres.

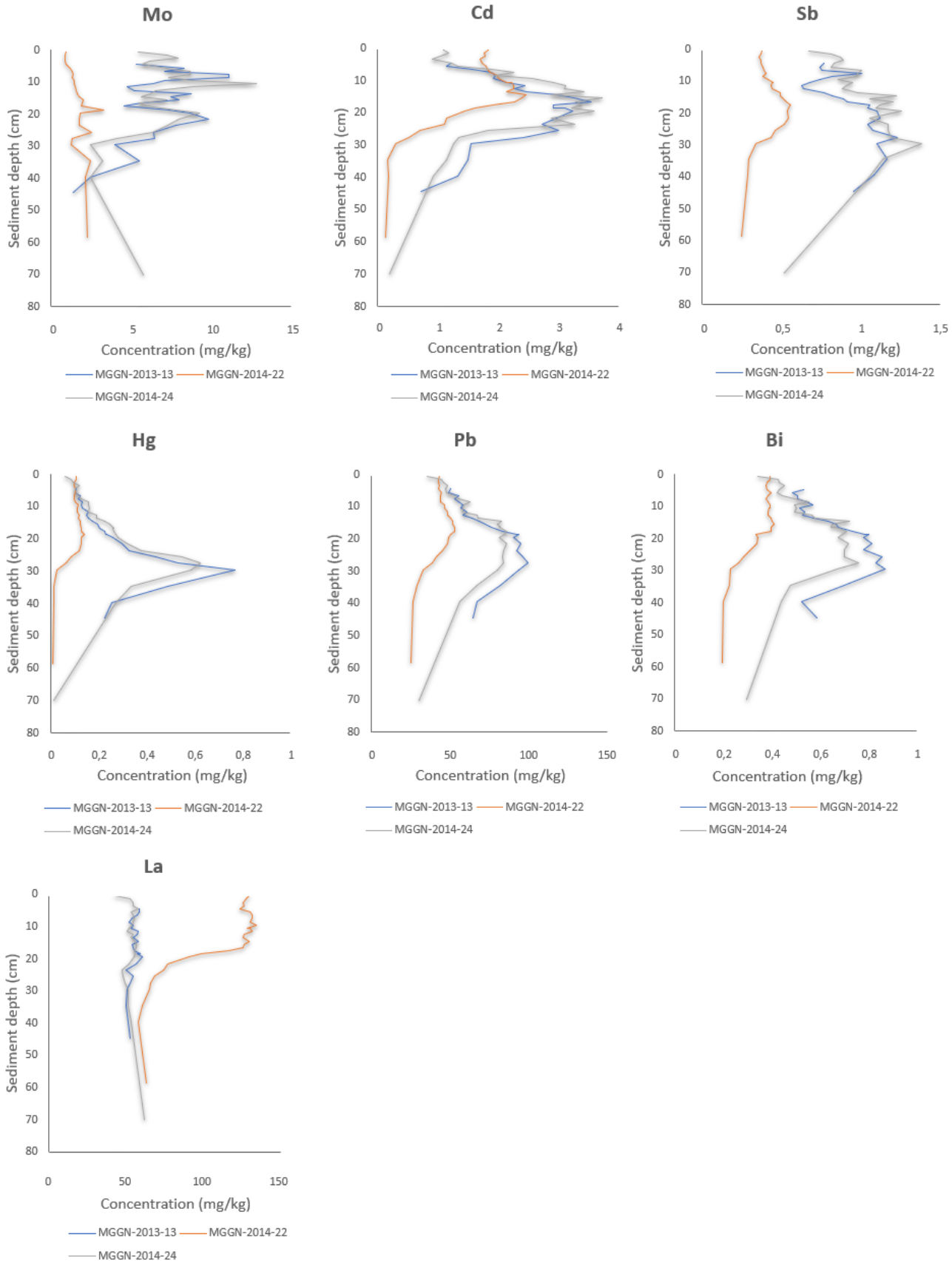

Figure 7. The concentrations of Mo, Cd, Sb, Hg, Pb, Bi and La in the cores MGGN-2013-13, MGGN-2014-22 and MGGN-2014-24.

Hg concentrations at cores MGGN-2013-13 and MGGN-2014-24 follow a similar trend (Figure 7). The increase became more rapid at certain point (39,5 cm for MGGN-2013-13 and 34,5 cm for MGGN-2014-24), until the concentrations reached their peak values of 0,769 mg/kg at 29,5 cm for core MGGN-2013-13, and for core MGGN-2014-24 0,624 mg/kg at 27,5 cm. After the peak, the concentrations began to decline towards the most recent sediments. The Hg concentration increase at MGGN-2014-22 is not as strong as at other two cores (the peak value of 0,14 mg/kg was reached at 18,5 cm), and the concentrations decline more slowly.

The same, general trend is observed in all the three cores for Pb concentration (Figure 7). The concentrations increased from the bottom of the core towards the top until a certain point. For cores MGGN-2013-13 and MGGN-2014-22, after reaching their peak values (100 mg/kg at 27,5 cm for core MGGN-2013-13 and 53,5 mg/kg at 17,5 cm for core MGGN-2014-22), the concentrations began to decrease. The concentration decrease was more rapid at core MGGN-2013-13 than at core MGGN-2014-22, where the concentration decreased gradually until 7,5 cm, and then remained at level of 43 mg/kg-45,1 mg/kg, which is higher than the initial concentration value of 25,3 mg/kg at 58,5 cm. In the case of MGGN-2014-24, the peak value is not as clearly seen as with other two cores. The concentration remained at level of 81 mg/kg - 86,6 mg/kg from 27,5 cm until 15,5 cm, after which point the concentration began to decrease.

The Bi concentration curves showed some similarities with the ones of Pb (Figure 7). The Bi concentrations reached their peak concentrations of 0,871 mg/kg at 29,5 cm at core MGGN-2013-13 and 0,761 mg/kg at 27,5 cm at core MGGN-2014-24. For the core MGGN-2014-22, the peak concentration is not that clear: however, it can be identified at 15,5 cm (0,409 mg/kg). After reaching the peak concentrations, the Bi concentrations of cores MGGN-2013-13 and MGGN-2014-24 started to decline, the concentrations measured at most recent sediments being below the initial concentrations. In the case of the core MGGN-2014-22, the concentration decline is gradual, and the concentration remained at level of 0,399 mg/kg - 0,376mg/kg from 12,5 cm until the most recent sediments. This level of concentration is significantly higher than the initial concentration of 0,198 mg/kg at 58,5 cm.

The elements of the lanthanide group have similar behaviour, here represented by La (Figure 7). The concentration changes are not great at MGGN-2013-13 and MGGN-2014-24. In contrary, the concentrations at core MGGN-2014-22 increase rapidly at certain point and remain at elevated levels after that. The concentrations at the most recent sediments are significantly higher than the concentrations measured at the bottom of the core, at sediment depth of 68,5 cm.

5.1.3. Degree of contamination

All measured Cd concentrations are below the PEL value of 4,2 mg/kg, but almost all the values exceed the ISQC level of 0,7 mg/kg (Figure 8). Only the concentrations at sediment depth 27,5 centimetres and above in core MGGN-2014-22 and one concentration measured in core MGGN-2014-24 do not exceed the ISQC level. Only one point is below the background value of 0,16 mg/kg (Table 1), all other measured values exceed the estimated background value.

All the Cr concentrations are well below the PEL value of 160 mg/kg (Figure 8). However, almost all concentrations exceed the ISQC value of 52,3 mg/kg. Only the concentrations measured at 25,5 centimetres and above in core MGGN-2014-22 and the most recent value in core the MGGN-2014-24 are below the ISQC level. All the concentrations measured from the core MGGN-2014-22 are below the background value of 69,4 mg/kg, whereas many concentrations in cores MGGN-2013-13 and MGGN-2014-24 exceed the background value. However, the concentrations in the most recent sediments are below the background value in all the cores.

In the case of Zn, most of the measured concentrations in cores MGGN-2013-13 and MGGN-2014-24 fall between the ISQC value of 124 mg/kg and the PEL value of 271 mg/kg (Figure 8). However, some concentrations between sediment depth of 20 – 30 centimetres in cores MGGN-2013-13 and MGGN-2014-24 exceed the PEL level. Concentrations measured between sediment depths 29,5 and 58,5 centimetres in core MGGN-2014-22 are below the ISQC level, but most of the concentrations exceed the PEL level. All measured concentrations from sediment depth of 17,5 centimetres until the most recent sediments exceed the PEL level in core MGGN-2014-22. All the concentrations measured from cores MGGN-2013-13 and MGGN-2014-24 exceed the background value of 120 mg/kg, and only the concentrations between 29,5 and 58,5 centimetres are below the background value in the core MGGN-2014-22.

Almost all the Pb concentrations fall between the ISQC value of 30,2 mg/kg and the PEL value of 112 mg/kg (Figure 9). Only three concentrations measured at sediment depths of 34,5, 39,5 and 58,5 centimetres are below the ISQC level. All the Pb concentrations exceed the background value of 24,0 mg/kg.

All the Cu concentrations fall between the ISQC value of 18,7 mg/kg and the PEL value of 108 mg/kg (Figure 9). Even the highest Cu concentrations in the core MGGN-2013-13 are well below the PEL level. Some Cu concentrations in the core MGGN-2014-22 are below the background value of 30,2

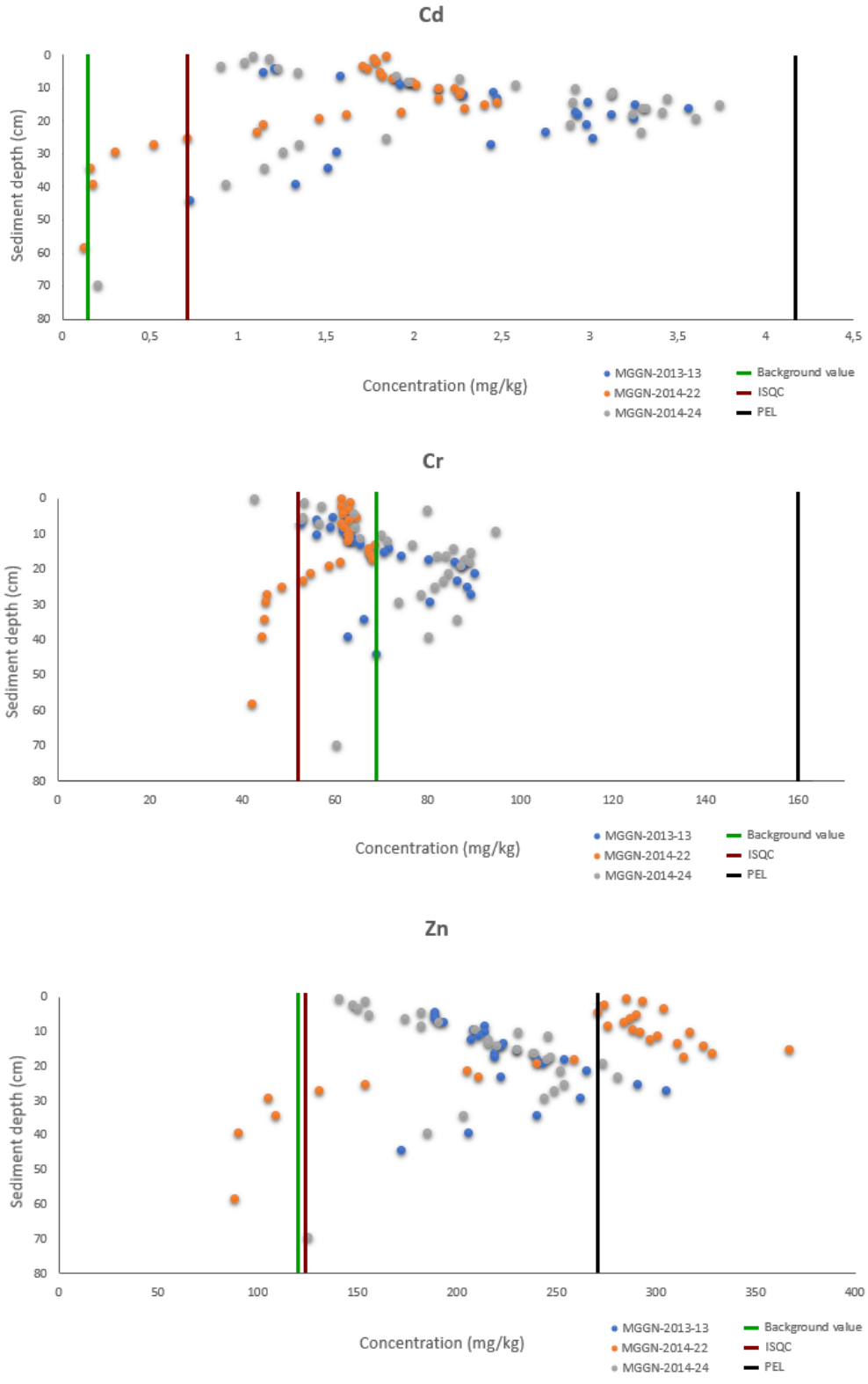

Figure 8. Some Zn concentrations exceed the PEL level, whereas all measured concentrations of Cd and Cr are below the PEL values. Most concentrations of Cd, Cr and Zn fall between the PEL and ISQC levels. Many Cr concentrations are below the background value, but only some Cd and Zn concentrations are below their natural levels.

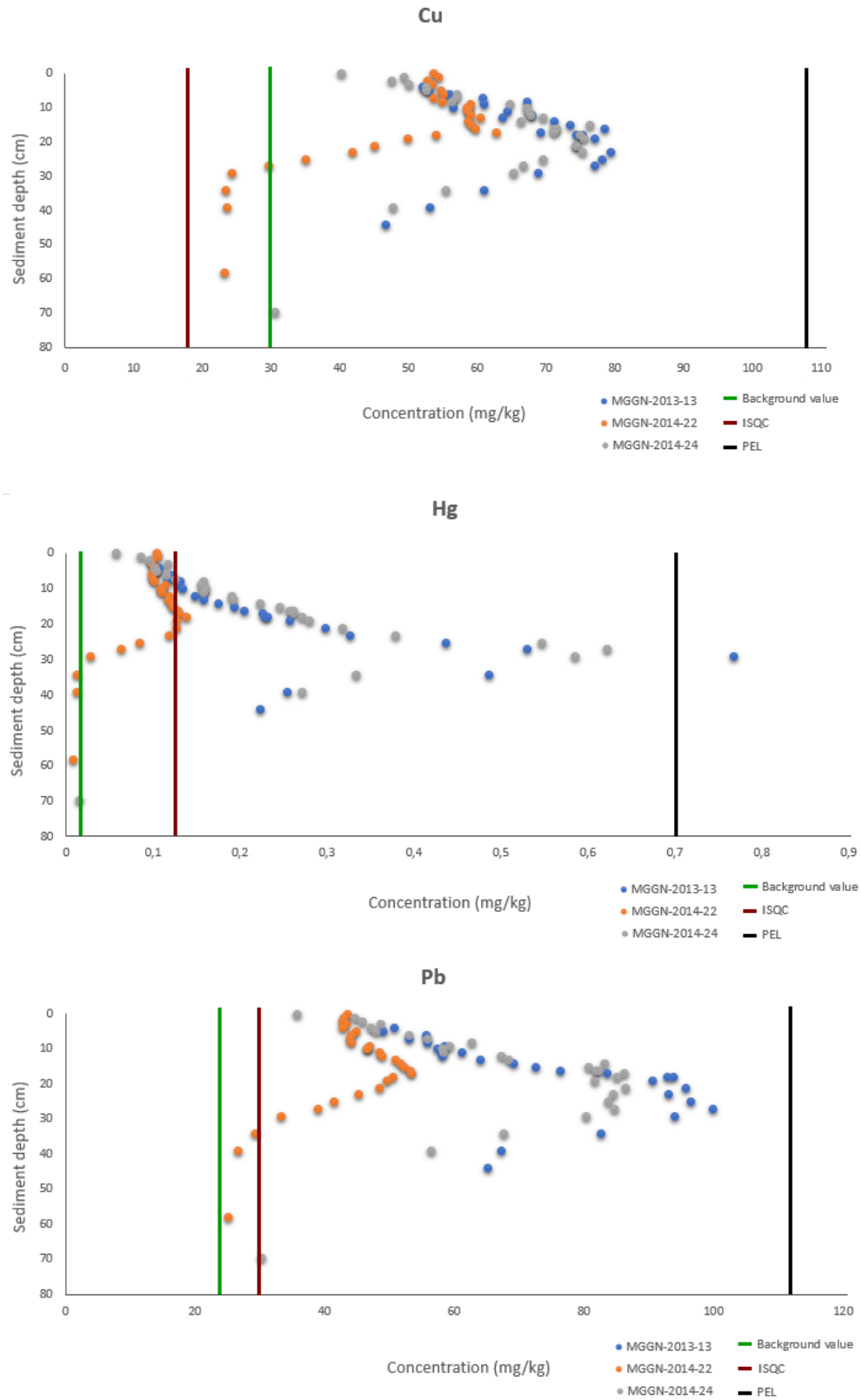

Figure 9. Most Pb and all Cu concentrations fall between the PEL and ISQC levels. One Hg concentration exceeds the PEL level, but several Hg concentrations are below the ISQC level and some concentrations measured from the deeper parts of the cores are below the background value. All the Pb and most Cu concentrations exceed the natural levels.

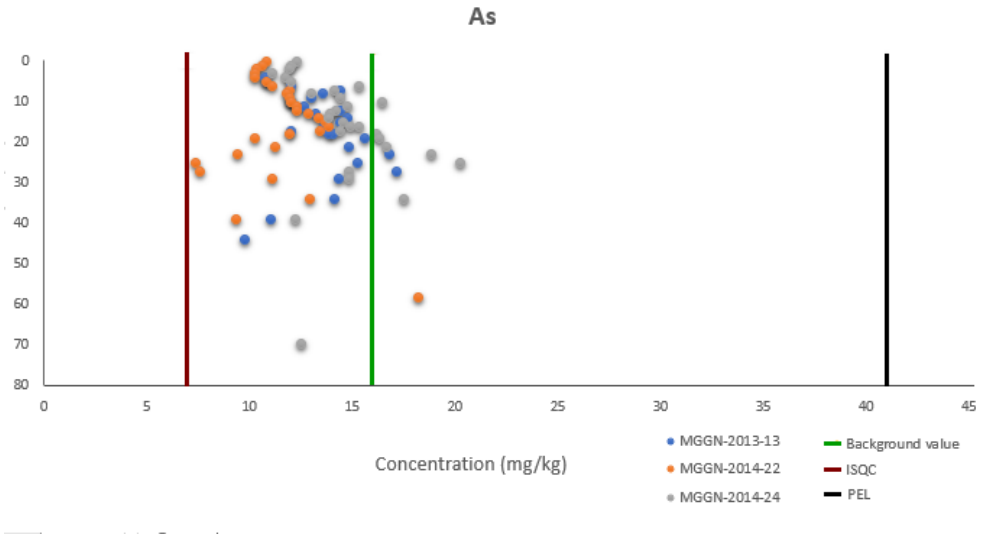

Figure 10. All As concentrations fall between the PEL and ISQC levels, and most As concentrations are below the background value.

mg/kg, whereas all the concentrations in the cores MGGN-2013-13 and MGGN-2014-22 exceed this value.

One Hg concentration at sediment depth of 29,5 centimetres in the core MGGN-2013-13 exceeds the PEL value of 0,7 mg/kg (Figure 9). Most concentrations in cores MGGN-2013-13 and MGGN-2014-24 fall between the PEL value and the ISQC value 0,13 mg/kg, and the most recent concentrations measured from these two cores are below the ISQC level. The Hg concentrations in the core MGGN-2014-22 rarely exceed the ISQC level, most concentrations being below this level. However, almost all the concentrations exceed the background value of 0,017 mg/kg.

All measured As concentrations fall between the PEL value of 7,24 mg/kg and the ISQC value of 41,60 mg/kg (Figure 10). All concentrations are well below the PEL level: The highest concentration measured was 20,3 mg/kg. Most As concentrations are also below the estimated background value of 16,4 mg/kg.

5.2. Surface sediments

5.2.1. Statistical analysis

The mean and median values along with standard deviation and the highest and lowest concentrations for each studied element are presented in table 3. These values are then compared to the background values by Vallius (2007), and the Canadian SQGs. The background values are available for Cr, Co, Ni, Cu, Zn, As, Cd, Hg and Pb. The SQGs have been estimated for Cr, Cu, Zn, As, Cd, Hg and Pb.

The median values of Cr, Co, Ni and As were below their background levels in the studied surface sediments, whereas Cu, Zn, Cd, Hg and Pb exceeded their estimated background levels. However, the highest concentrations measured for Cr, Co, Ni and As clearly exceeded the background level.

The mean and median values of any studied element did not exceed the PEL level. However, the maximum concentrations of Zn and As did exceed their PEL levels. The mean and median values of Hg were below the ISQC level, whereas other elements exceeded their ISQC levels in the studied sediments.

The comparison of the correlation coefficients shows that all the studied metals, except Mn, were positively correlated with clay (Table 4). Most metals were also positively correlated with silt, but the correlation coefficients were higher between metals and clay than between metals and silt. All the studied metals, except Mn, were negatively correlated with sand.

C shows moderate positive correlation ($r > 50$) with Co, Cd and Sb, and strong positive correlation ($r > 70$) with V, Cr, Fe, Ni, Cu, Zn and Pb. Only Mn shows negative correlation with C.

Some studied metals show highly positive correlation with each other. The highest correlation coefficients were found between V and Cr ($r = 97$), V and Ni ($r = 0,94$), V and Cu ($r = 0,91$), Co and Ni ($r = 0,93$), Fe and Co ($r = 0,90$), V and Fe ($r = 0,89$), Fe and Ni ($r = 0,88$), V and Co ($r = 0,87$), Ni and Cu (0,87), Co and Zn ($r = 0,86$), Cu and Zn ($r = 0,85$), Cu and Pb ($r = 0,83$), Ni and Zn ($r = 0,83$), Fe and Cu ($r = 0,81$), Cr and Co (0,81), V and Zn ($r = 0,80$), Fe, and Zn ($r = 0,80$), Cr and Zn (0,80), and Cr and Fe ($r = 0,80$).

	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Hg	Pb	La	Bi
Mean	58,26	55,22	877,12	35107,23	11,51	28,32	40,61	164,23	10,01	2,21	1,27	0,64	0,12	43,81	60,09	0,79
Median	66,6	62,8	485	40500	12	32	47,4	169	9,52	1,27	1,11	0,44	0,11	41,7	59,5	0,46
SD	27,19	24,83	1447,28	15656,07	5,07	14,04	19,06	58,53	7,77	1,91	0,64	0,51	0,09	10,98	18,40	2,38
Min	11,1	10,4	189	6030	<5	<5	6,4	29,3	1,98	<0,6	0,17	0,15	0	24,8	26,9	0,09
Max	105	96,9	11600	72300	25,3	63,7	70,7	310	48,5	8,24	2,74	2,64	0,46	69,9	133	22
Back-ground level	N/A	69,4	N/A	N/A	15,6	34,9	30,2	120	16,4	N/A	0,16	N/A	0,017	24,0	N/A	N/A
ISQC	N/A	52,3	N/A	N/A	N/A	N/A	18,7	124	7,24	N/A	0,70	N/A	0,13	30,2	N/A	N/A
PEL	N/A	160	N/A	N/A	N/A	N/A	108	271	41,6	N/A	4,2	N/A	0,70	112	N/A	N/A

Table 3. The concentrations of the studied elements in the surface sediments are compared to the background levels estimated by Vallius (2007) and the Canadian sediment quality guideline values ISQC and PEL (CCME 2002). The values are presented in mg/kg.

	Sand	Silt	Clay	C	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Hg	Pb	Bi
C	-0,88	0,30	0,99																
V	-0,88	0,31	0,98	0,81															
Cr	-0,91	0,41	0,97	0,82	0,97														
Mn	0,12	-0,34	-0,08	-0,11	-0,05	-0,16													
Fe	-0,86	0,26	0,97	0,70	0,89	0,80	0,19												
Co	-0,84	0,25	0,95	0,67	0,87	0,81	0,24	0,90											
Ni	-0,84	0,30	0,92	0,77	0,94	0,91	0,06	0,88	0,93										
Cu	-0,92	0,41	0,97	0,90	0,91	0,93	-0,11	0,81	0,79	0,87									
Zn	-0,82	0,23	0,95	0,77	0,80	0,80	0,04	0,80	0,86	0,83	0,85								
As	-0,64	-0,04	0,86	0,29	0,35	0,20	0,63	0,66	0,52	0,37	0,31	0,36							
Mo	-0,50	-0,15	0,70	0,44	0,27	0,17	0,52	0,39	0,39	0,26	0,28	0,32	0,64						
Cd	-0,84	0,32	0,93	0,57	0,33	0,41	0,00	0,24	0,32	0,29	0,54	0,58	0,17	0,38					
Sb	-0,64	0,14	0,76	0,61	0,47	0,44	0,22	0,45	0,45	0,40	0,54	0,45	0,44	0,52	0,60				
Hg	-0,85	0,45	0,88	0,47	0,56	0,61	-0,08	0,56	0,48	0,55	0,67	0,53	0,19	0,01	0,15	0,25			
Pb	-0,79	0,23	0,91	0,72	0,66	0,68	0,03	0,60	0,61	0,62	0,83	0,69	0,38	0,42	0,72	0,64	0,63		
Bi	-0,69	0,10	0,87	0,18	0,13	0,13	0,02	0,13	0,09	0,09	0,16	0,09	0,15	0,03	0,15	0,25	0,06	0,14	
La	-0,77	0,74	0,58	0,38	0,51	0,51	-0,07	0,58	0,61	0,62	0,55	0,67	0,21	-0,17	0,18	-0,00	0,40	0,33	-0,01

Table 4. The correlation coefficients for sand, silt, clay, C and metals show positive correlations between clay and all the metals and C. C shows relatively strong positive correlation with some metals (V, Cr, Fe, Co, Ni, Cu, Zn, Cd, Sb, Pb). Some metals show highly positive correlation with each other – the highest correlation was measured between V and Cr (r = 0,97).

5.2.2. Horizontal distribution

The highest C concentrations were measured in the surface sediments of Mustamaa and Itäsyvä (Figure 11). The Ravijoki and Parlahti sediments, and the sites near Rakin Kotka and Ristisaari showed rather high C concentrations as well. The lowest concentrations were measured in Kauholma, Ulko-Tammio, Luodematalat and Klamila.

The lowest V concentrations, less than 25,00 mg/kg, were measured near Klamila, Kauholma, Ulko-Tammio and in the off-shore location, Luodematalat (Figure 12). The concentrations in other sites were relatively evenly distributed throughout the study area, without any visible trend in east-west direction. The highest V concentrations were measured both in the eastern and western parts of the area. In the east, the highest concentrations were discovered in Mustamaa and Itäsyvä, reaching up to 105 mg/kg. Concentrations over 100 mg/kg were measured in the western parts of the study area, too; high concentrations were reached at two sites between Loviisa and Porvoo and on the site west of Porvoo. Most concentrations measured in Itäsyvä were above 70 mg/kg, but one site showed a concentration as low as 16,30 mg/kg.

Low Cr concentrations were measured at different sites (Figure 13). The lowest concentrations, less than 23,00 mg/kg, were found in Kauholma, Ulko-Tammio, east of Ristisaari and Luodematalat. Low concentrations were also measured near Klamila and near Rakin Kotka. The highest Cr concentrations, above 82,00 mg/kg, were measured in Mustamaa and Itäsyvä, but also at sites between Porvoo and Loviisa and in the site west of Porvoo. One site in Itäsyvä showed a relatively low concentration: 17,20 mg/kg, while all other sites here showed concentrations above 70,00 mg/kg.

The lowest Mn concentrations, less than 420,00 mg/kg, were measured at coastal areas in Klamila and Ravijoki, but also in Kauholma, Itä-Syvä, Ulko-Tammio, near Rakin Kotka and Suuri Musta. In general, the Mn concentrations appeared relatively low near the coast, and in the sea area between Hamina and Kotka (Figure 14). However, some sites in Klamila and Kauholma showed higher concentrations than other sites in those areas. The concentrations in Ulko-Tammio, Itäsyvä and near Rakin Kotka showed variability, too. Highest Mn concentrations were found east of Ristisaari, reaching up to 11 600 mg/kg.

The Fe concentrations showed lowest concentrations, less than 15 000 mg/kg at some eastern sites (Kauholma, Klamila, Ulko-Tammio) and Luodematalat (Figure 15). Concentrations less than 30 000 mg/kg were measured in Kauholma and Klamila. At other sites, the concentrations appeared relatively evenly distributed. The highest concentration was measured south-east of Suuri Musta (72 300

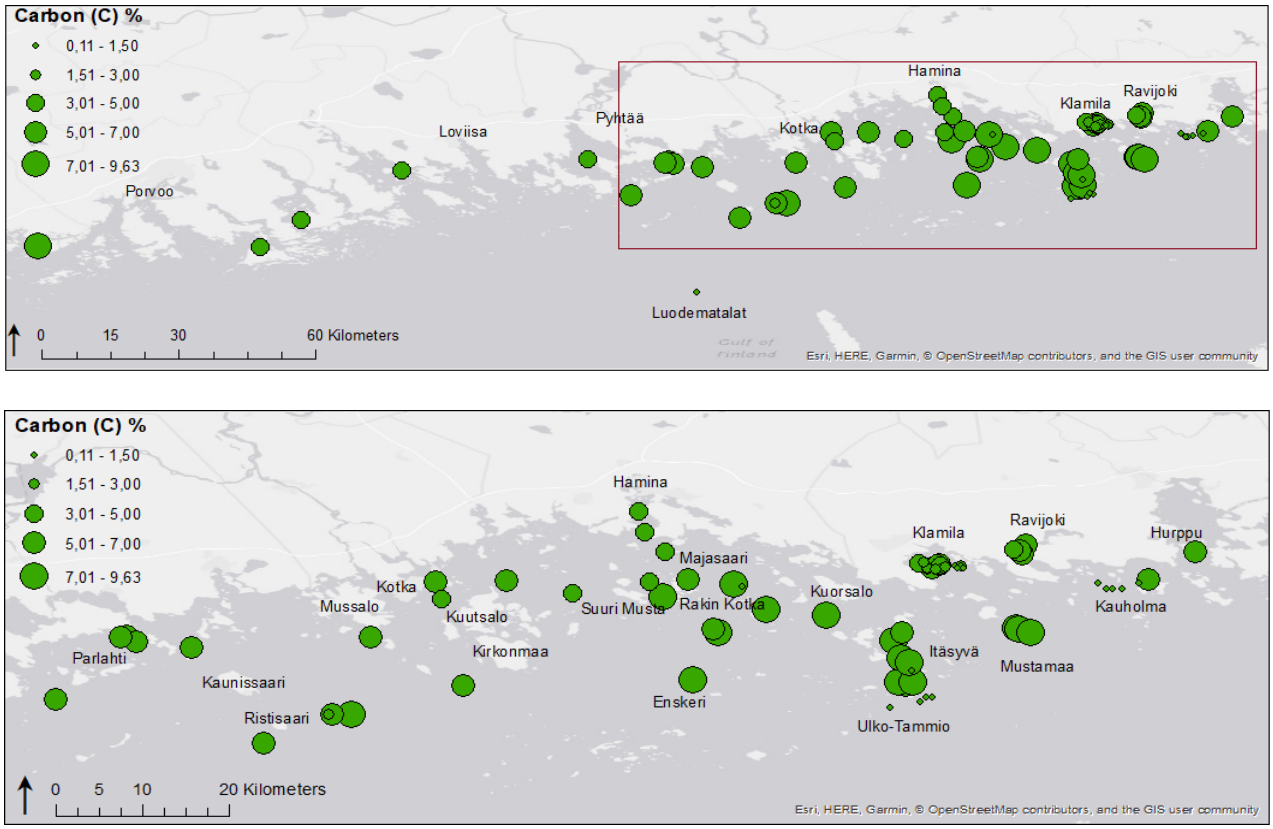

Figure 11. The highest C concentrations were measured in Itäsyvä and Mustamaa, while lowest concentrations were found in Kauholma, Ulko-Tammio and Luodematalat.

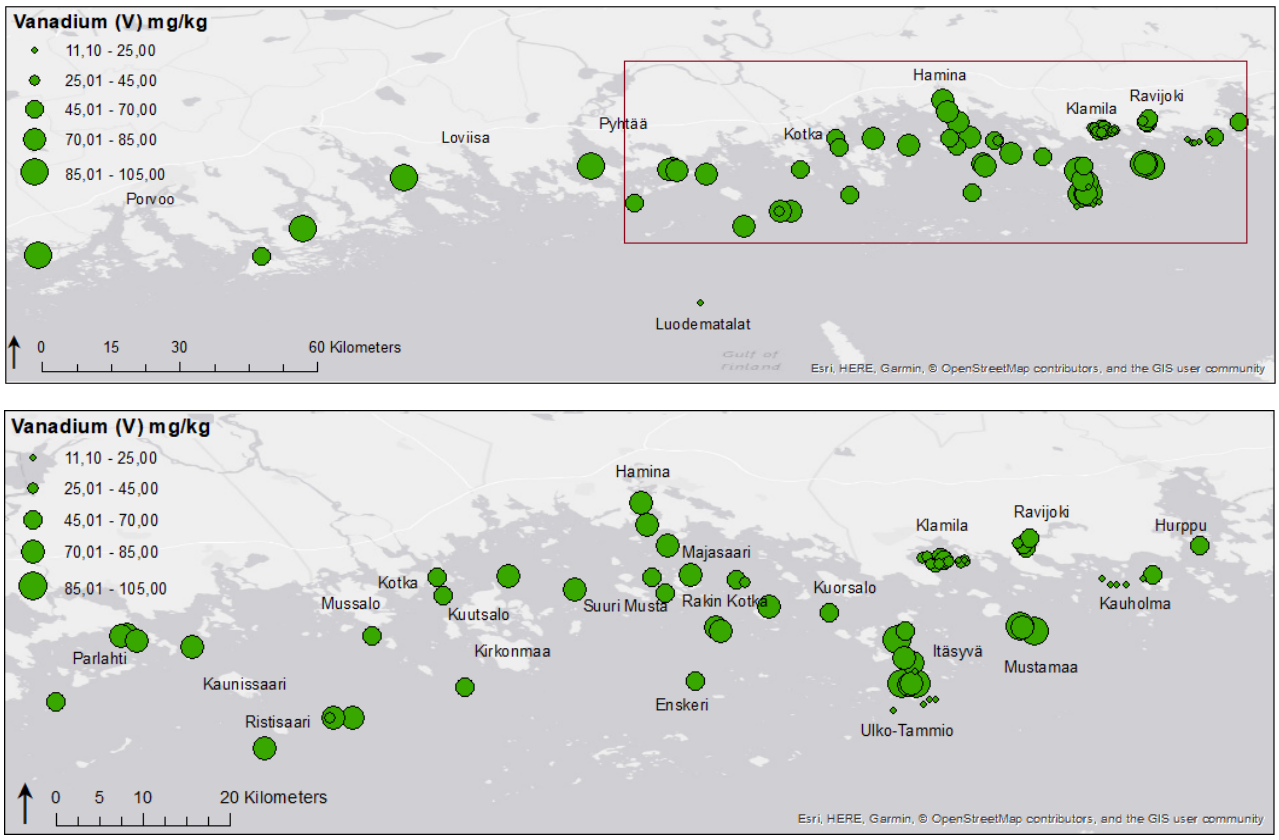

Figure 12. The lowest V concentrations were revealed in the eastern parts of the study area, while the highest concentrations were measured both in the eastern and western parts.

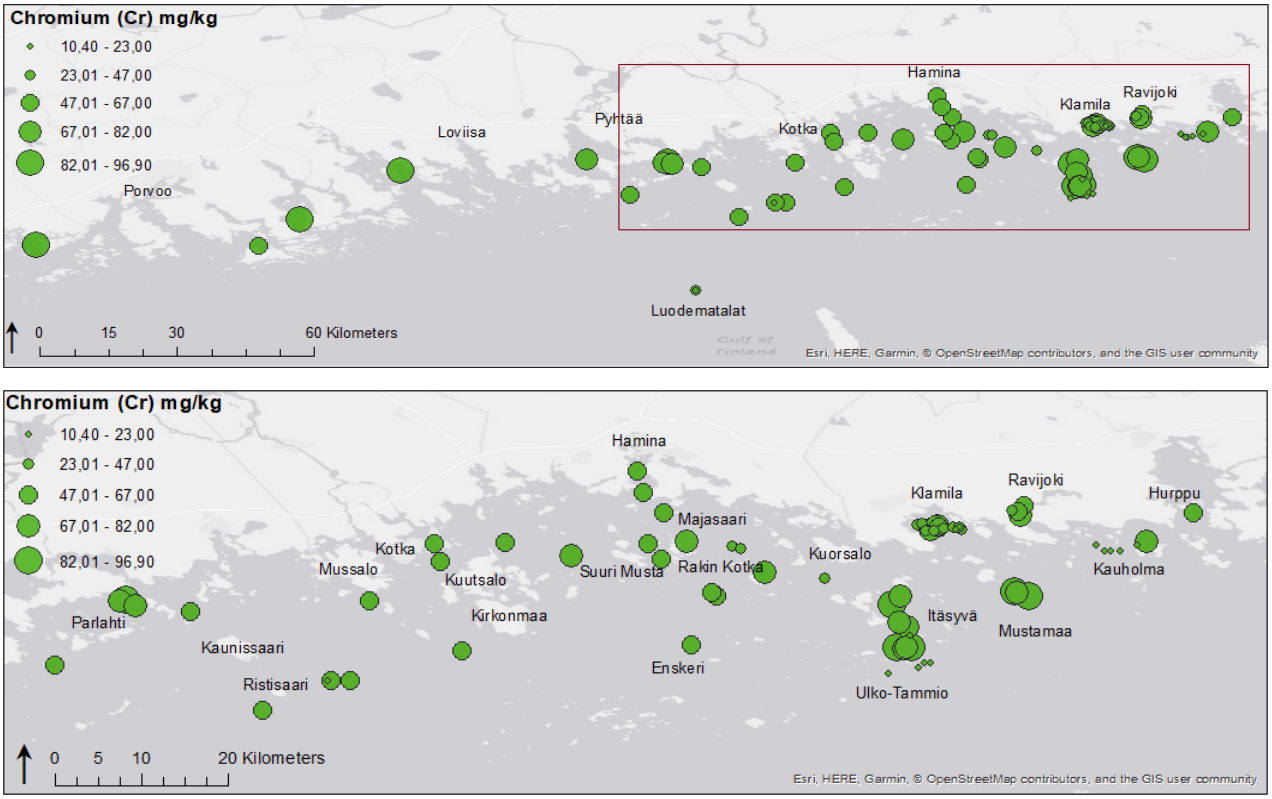

Figure 13. The lowest Cr concentrations were found in the eastern part of the study area, while highest concentrations were measured both in the east and west.

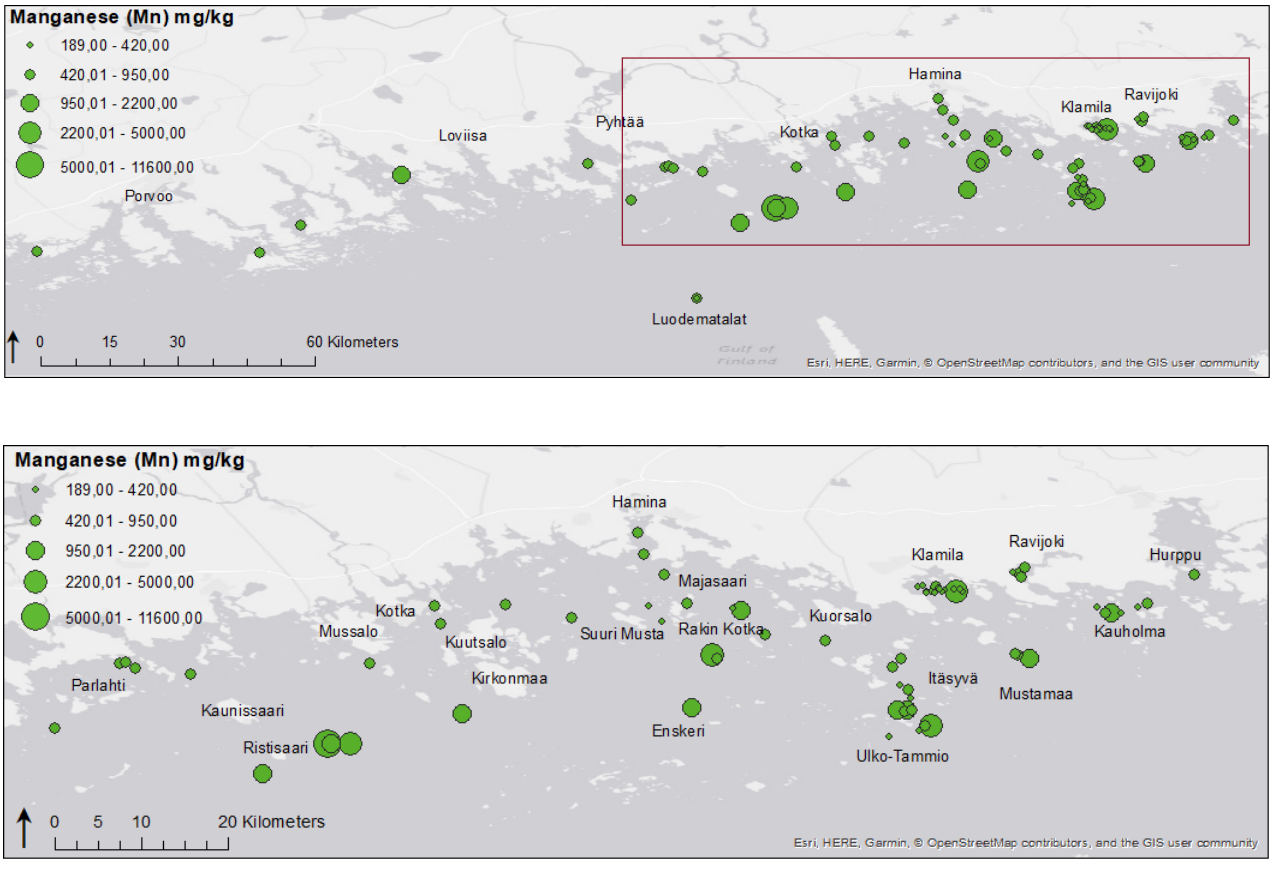

Figure 14. Mn concentrations near coast were mostly low, while higher concentrations appeared away from the coast.

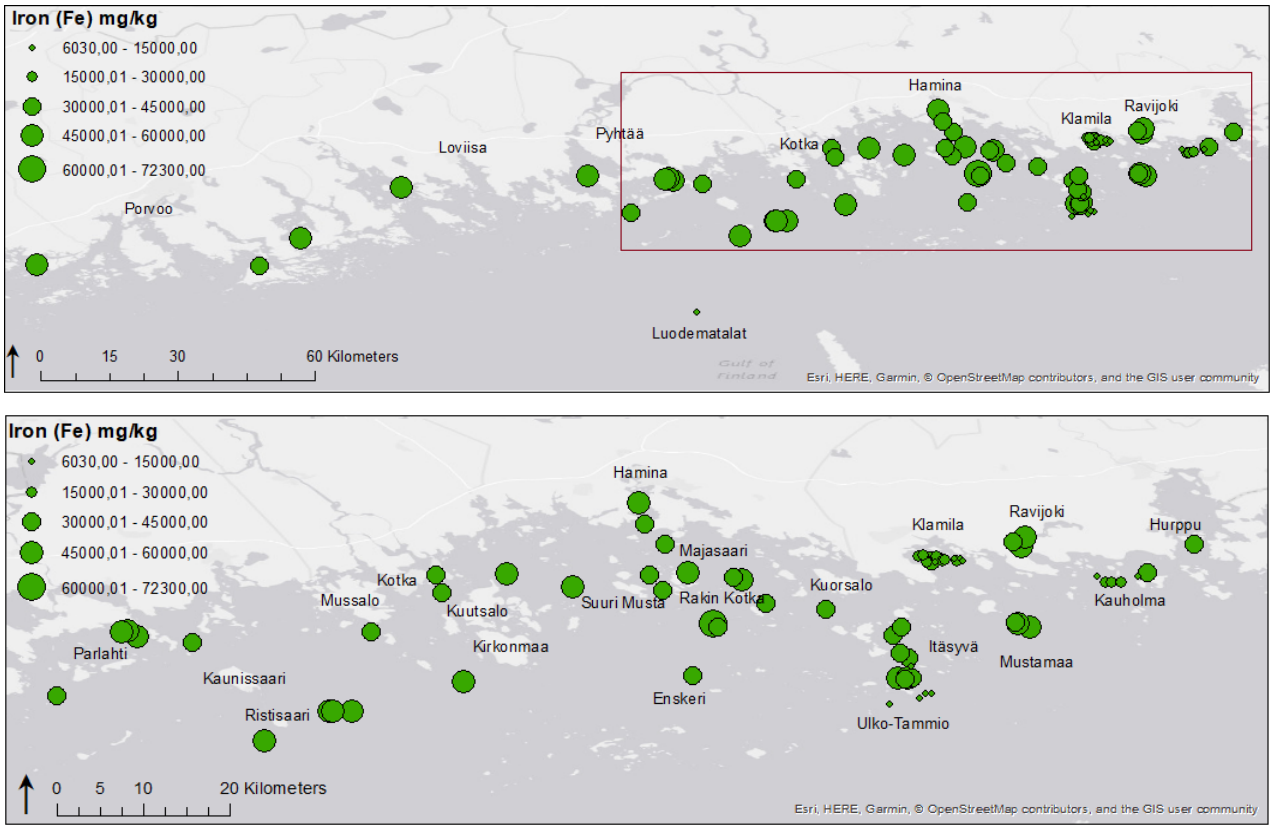

Figure 15. The lowest Fe concentrations were measured on eastern sites and highest concentration in the west. Fe appears relatively evenly distributed between most sites.

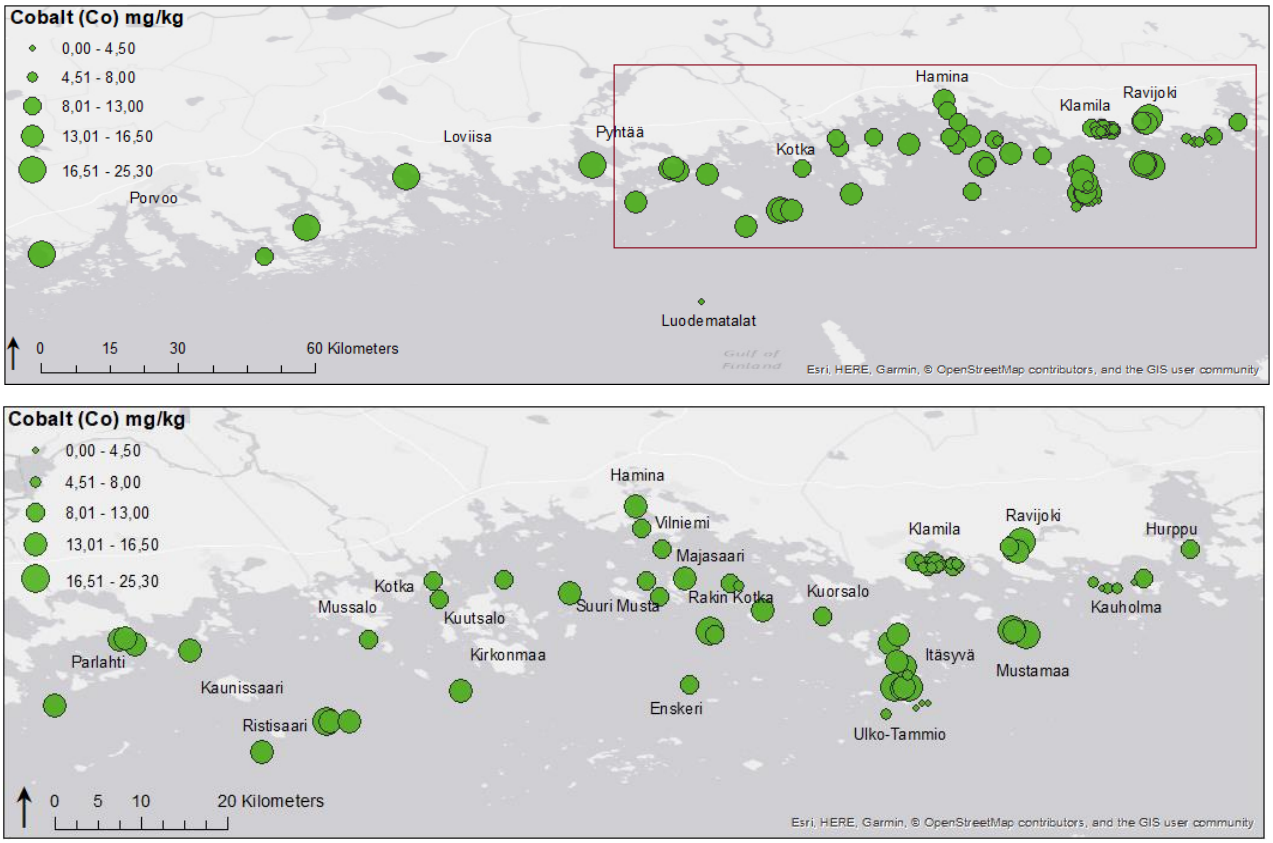

Figure 16. The lowest Co concentrations were measured in the eastern parts of the area and off-shore, while highest concentrations appeared both in the east and west.

mg/kg). The highest variations in concentrations was discovered in Itäsyvä, where the lowest concentration was 11 000 mg/kg and the highest 51 900 mg/kg.

The lowest Co concentrations, less than 4,50 mg/kg, were measured in Kauholma, Ulko-Tammio and Luodematalat (Figure 16). Some sites in the eastern part of the study area showed low concentrations of less than 8,00 mg/kg (Ulko-Tammio, Kauholma, Klamila). Highest Co concentrations, above 16,50 mg/kg, appeared in Ravijoki, Mustamaa and Itäsyvä, but also in the western parts of the study area. Hence, no concentration increase towards east was observed in the horizontal distribution pattern.

The lowest Ni concentrations, less than 10,00 mg/kg, appeared in Kauholma, Ulko-Tammio and Luodematalat (Figure 17). The concentrations measured in Itäsyvä show rather large variability; the highest concentration (63,70 mg/kg) was measured here, and all but one (6,81 mg/kg) concentrations were above 30,00 mg/kg. Some variability in Ni concentrations could be seen in the sediments of Kauholma and Ravijoki too. The Ni concentrations were relatively evenly distributed between other sites. High concentrations (above 42,00 mg/kg) appeared in Ravijoki, Itäsyvä and western parts of the study area.

The sampling sites in Ulko-Tammio and Luodematalat, all but one site in Kauholma and some sites in Klamila showed the lowest Cu concentrations, less than 16,00 mg/kg (Figure 18). Other sites in Klamila showed relatively low concentrations, too - less than 32,00 mg/kg. The surface sediments in Ravijoki, Kauholma, Itäsyvä and west of Ristisaari showed variability in the Cu concentrations. The highest Cu concentrations, above 57,00 mg/kg, were measured in Mustamaa, Itäsyvä and Parlahti. In general, the concentrations in the east appeared slightly higher than the concentrations in the west.

The lowest Zn concentrations, less than 90,00 mg/kg, were discovered in Kauholma, Ulko-Tammio and Luodematalat (Figure 19). Relatively low concentrations, less than 140,00 mg/kg, were also discovered in Klamila, Suuri Musta and near Rakin Kotka. The highest concentrations, above 250,00 mg/kg, were measured in Ravijoki. High concentrations (above 190,00 mg/kg) also appeared in Mustamaa, Itäsyvä and south-west of Rakin Kotka, but also in Parlahti and some western sites.

In general, the As concentrations near the coast appeared lower than the concentrations measured further. The highest As concentrations, above 25,00 mg/kg, were found east of near Rakin Kotka and around Ristisaari (Figure 20). The lowest concentrations, under 5,00 mg/kg were measured in Ulko-Tammio, Klamila and Kauholma. Low As concentrations were also discovered in Luodematalat and some sites in the sea area between Kotka and Hamina, and between Loviisa and Porvoo. As

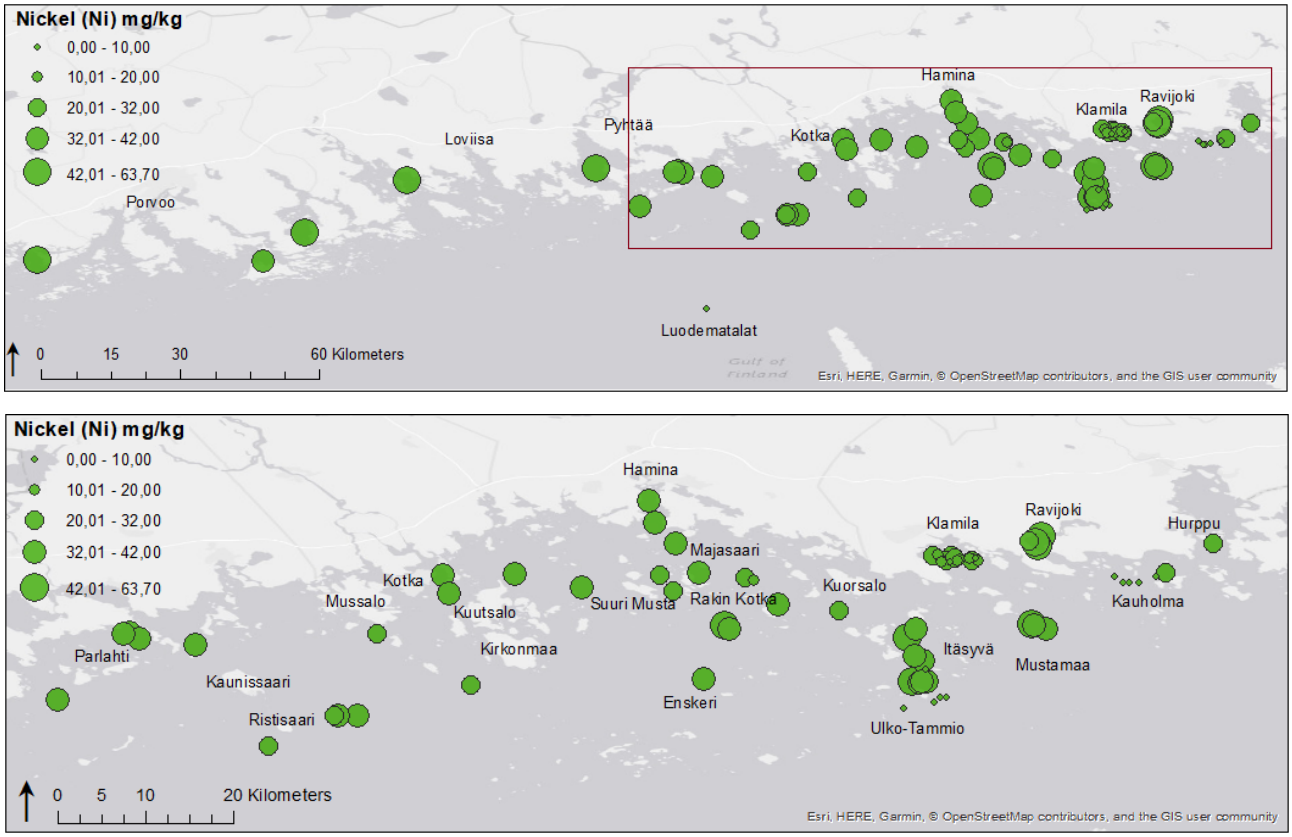

Figure 17. The lowest Ni concentrations were measured in the eastern parts of the study area and off-shore, while highest concentrations appear both in the east and west.

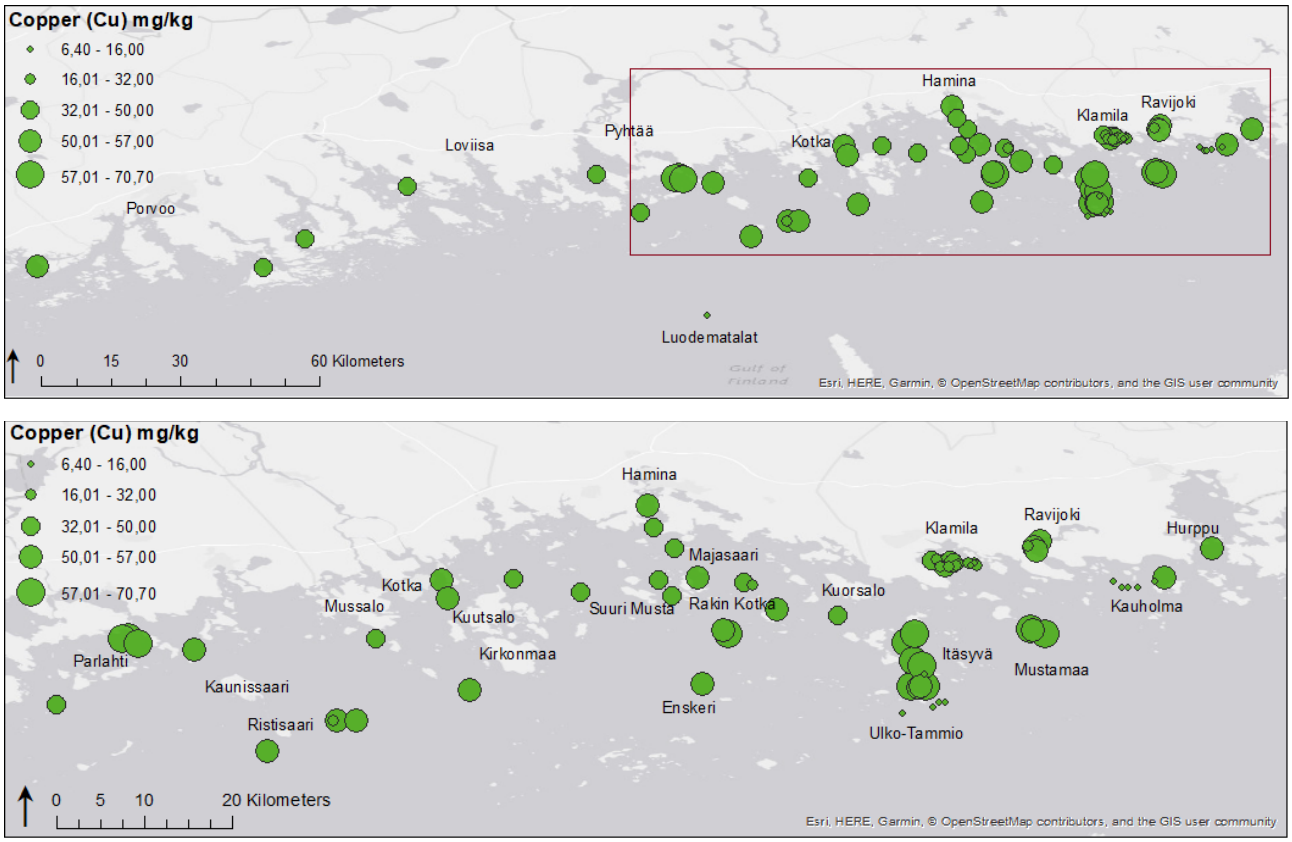

Figure 18. Both highest and lowest Cu concentrations were measured in the eastern parts of the study area.

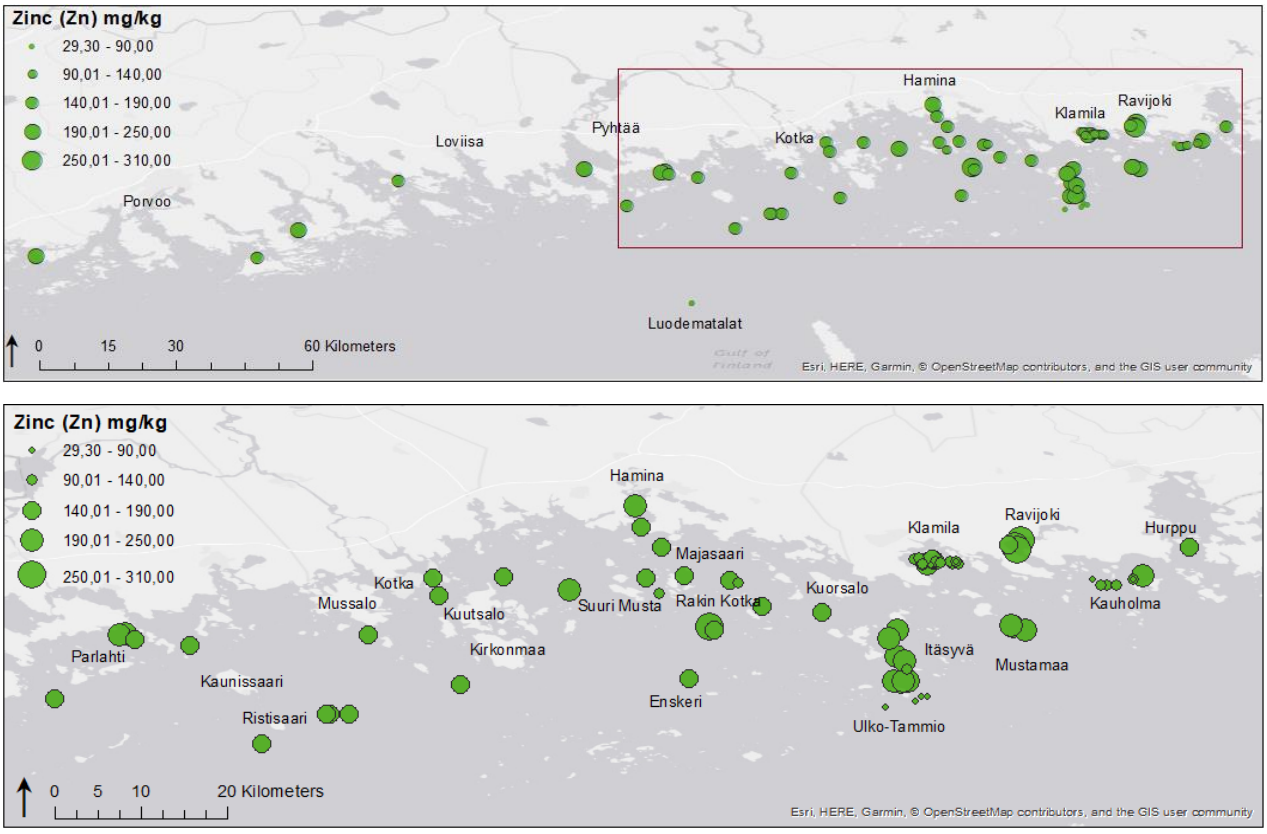

Figure 19. The lowest Zn concentrations were measured in the eastern parts of the study area and off-shore. The highest concentrations also appeared in the east, the western concentrations appearing only slightly lower.

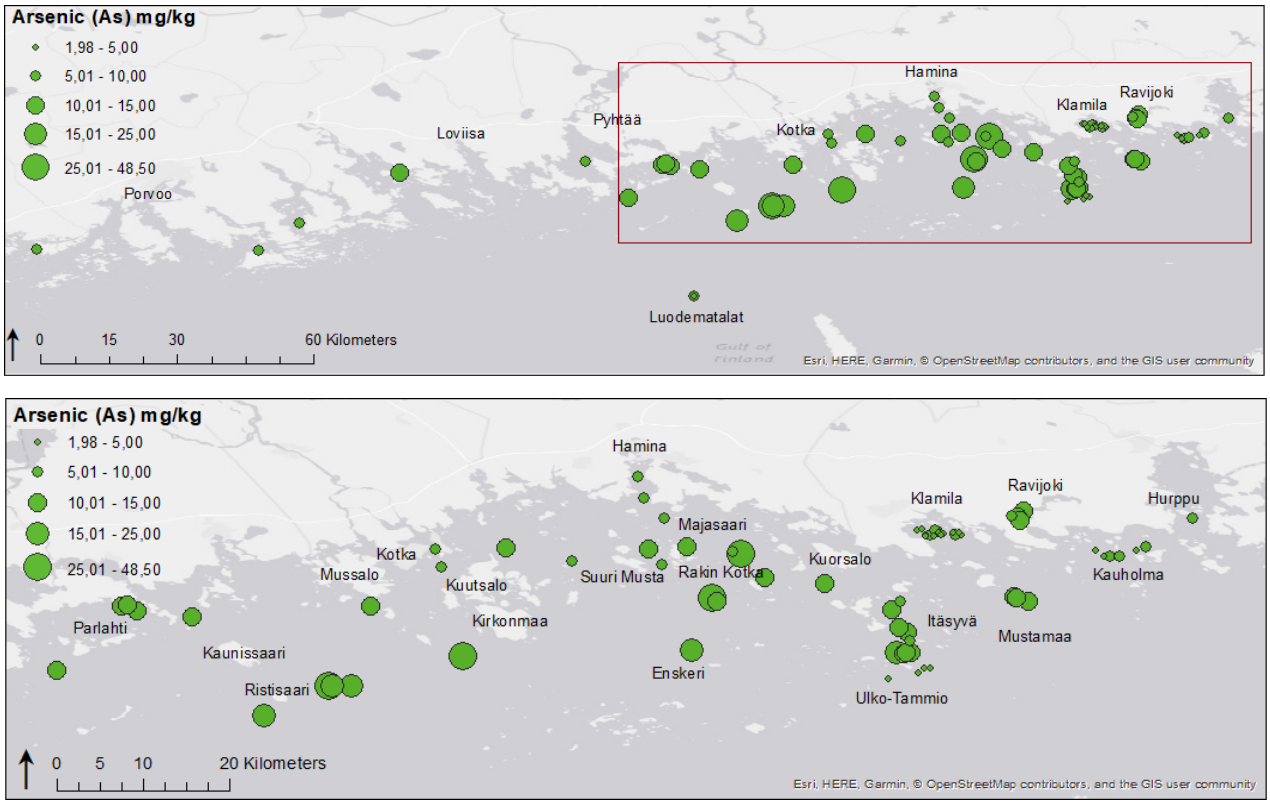

Figure 20. The lowest As concentrations were found in the eastern parts of the study area, highest concentrations being measured further away from the coast.

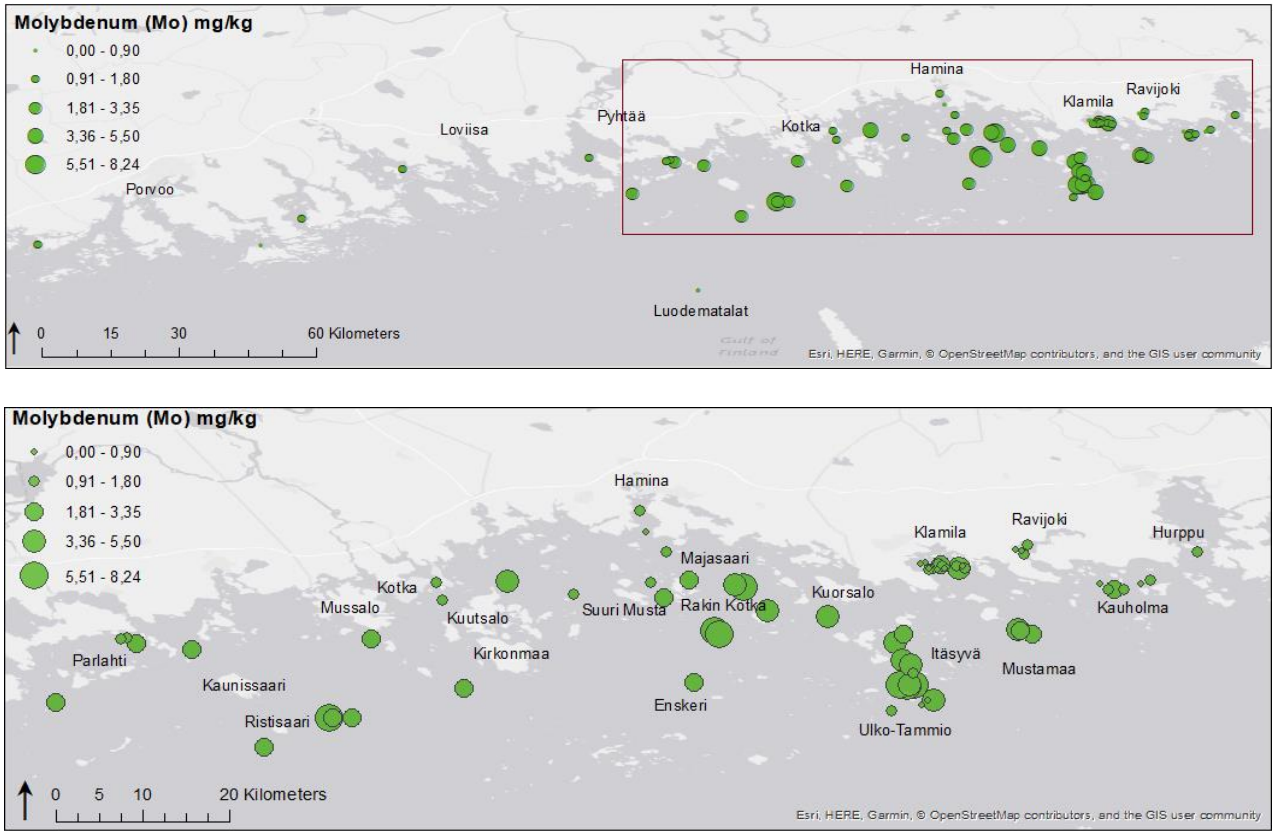

Figure 21. Mo concentrations appeared lower near the coast than further Gulf.

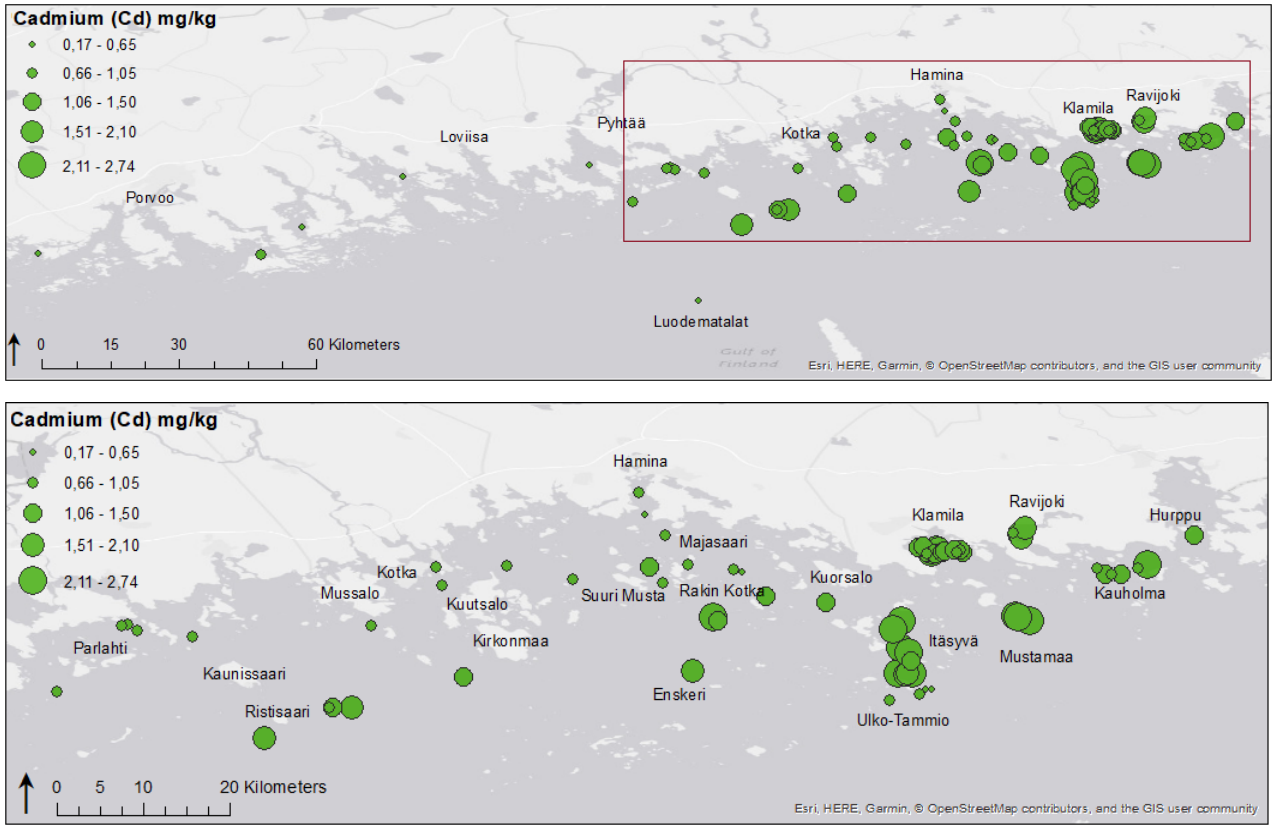

Figure 22. The Cd concentrations appear higher in the east than in the west.

concentrations in Ravijoki and Itäsyvä showed some variability, as well as the concentrations on the sea area between Kotka and Hamina.

The Mo concentrations appeared lower near the coast than further Gulf (Figure 21). The lowest concentrations, under 0,90 mg/kg, were measured in Klamila, Ravijoki, Kauholma, Ulko-Tammio, near Hamina, Luodematalat and east of Porvoo. High concentrations, above 5,50 mg/kg, were discovered in Itäsyvä and around Rakin Kotka. The highest concentration (8,24 mg/kg) was measured near Ristisaari.

In general, Cd showed higher concentrations in the surface sediments in the eastern parts of the study area (Figure 22). At some extent, the concentrations measured near coast appeared lower than the concentrations measured further away from the coast. The distribution pattern showed an increasing trend towards east. The lowest Cd concentrations, less than 0,65 mg/kg, were measured in Ulko-Tammio, Luodematalat, south of Hamina, east of Majasaari and the western parts of the study area. The highest concentrations, above 2,11 mg/kg, were found in Kauholma, Mustamaa, Itäsyvä and south-west of Rakin Kotka.

The Sb concentrations appeared higher in the east than in the west, and lower in the coastal areas compared to the sites further away from the shoreline (Figure 23). The highest Sb concentrations, above 1,35 mg/kg, were measured in Mustamaa, Itäsyvä and around Ristisaari. The concentrations in Klamila were low in general, except high concentration was discovered at one site. The lowest Sb concentrations, less than 0,30 mg/kg, were found in Klamila, Kauholma and Ravijoki, but also at one site both in Ulko-Tammio and Itäsyvä.

The highest Hg concentrations, above 0,26 mg/kg, were measured near Kotka, Parlahti and west of Parlahti (Figure 24). The lowest Hg concentrations, less than 0,03 mg/kg, were measured in Kauholma, Ulko-Tammio, east of Majasaari and Luodematalat. One site in Itäsyvä showed a low concentration, too. All the concentrations west of Loviisa showed concentrations less than 0,15 mg/kg.

In general, the Pb concentrations appeared higher in the east than in the west (Figure 25). However, the lowest concentrations, less than 32,00 mg/kg, were measured in Klamila, Kauholma, Ulko-Tammio and Itäsyvä, as well as in Luodematalat. The Kauholma and Itäsyvä sediments showed some variability in the Pb concentrations. The concentrations in the western sites were less than 40,50 mg/kg. The highest concentrations, above 60,00 mg/kg, were discovered in Itäsyvä, Mustamaa and north-east of Kauholma.

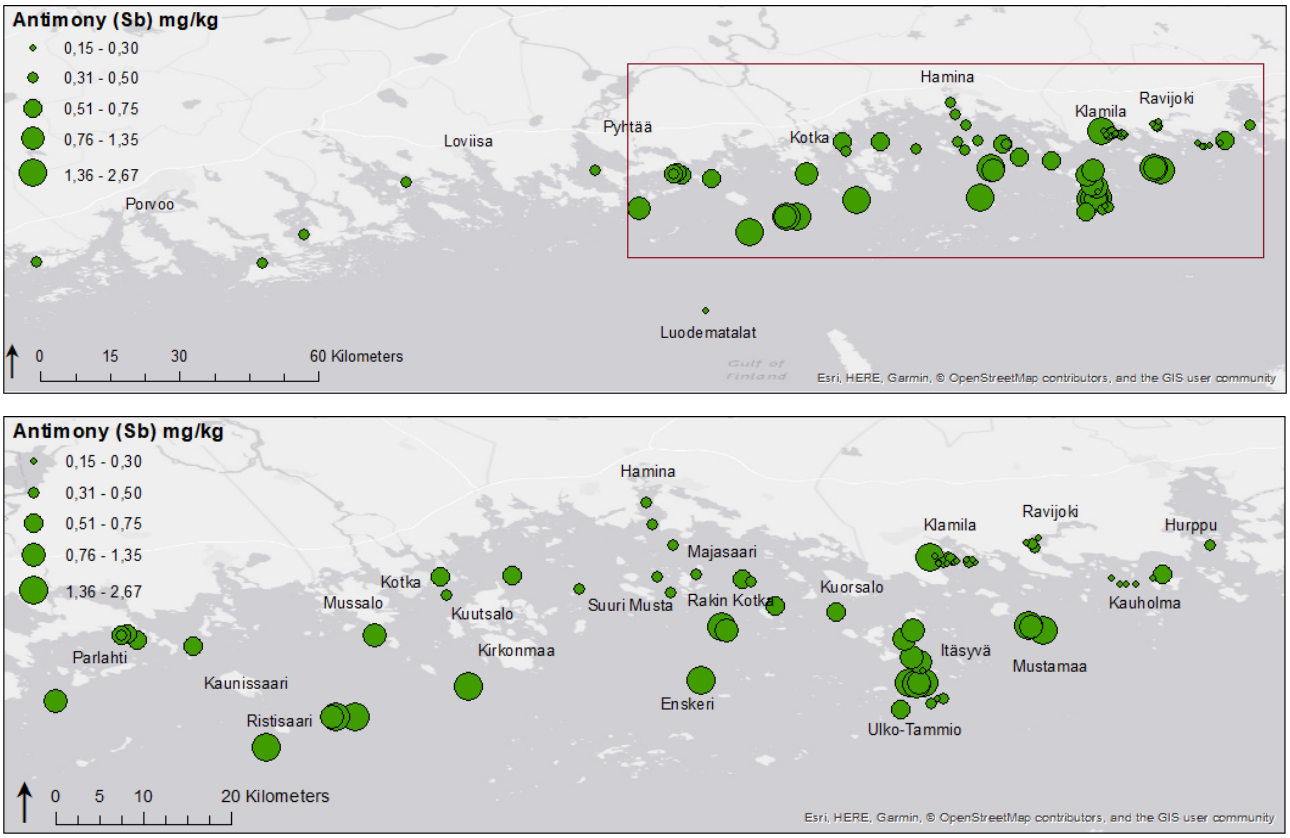

Figure 23. The Sb concentrations were higher in the east than west, and rather low near the shoreline.

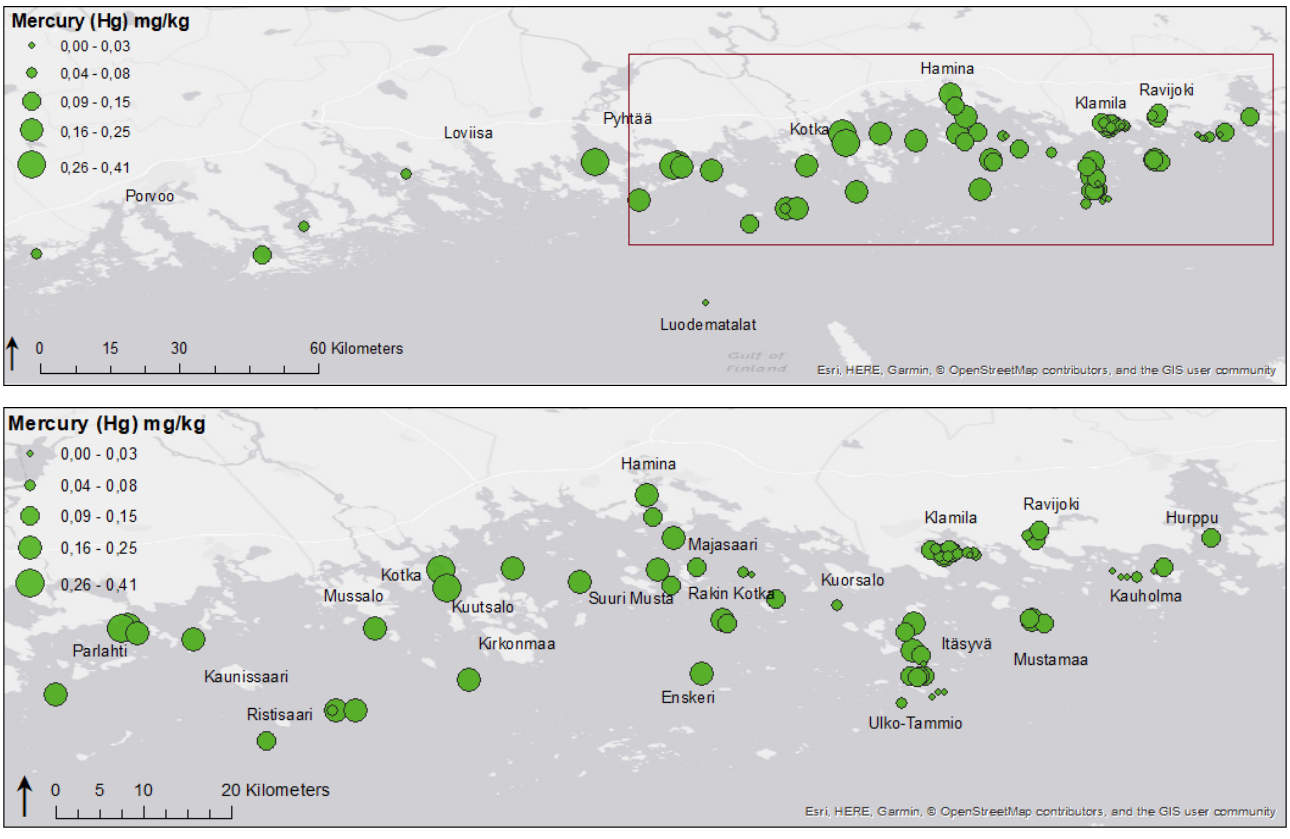

Figure 24. The western sites showed concentrations less than 0,15mg/kg, however, the lowest concentrations were measured at eastern sites. The highest concentrations were found near Kotka and Parlahti.

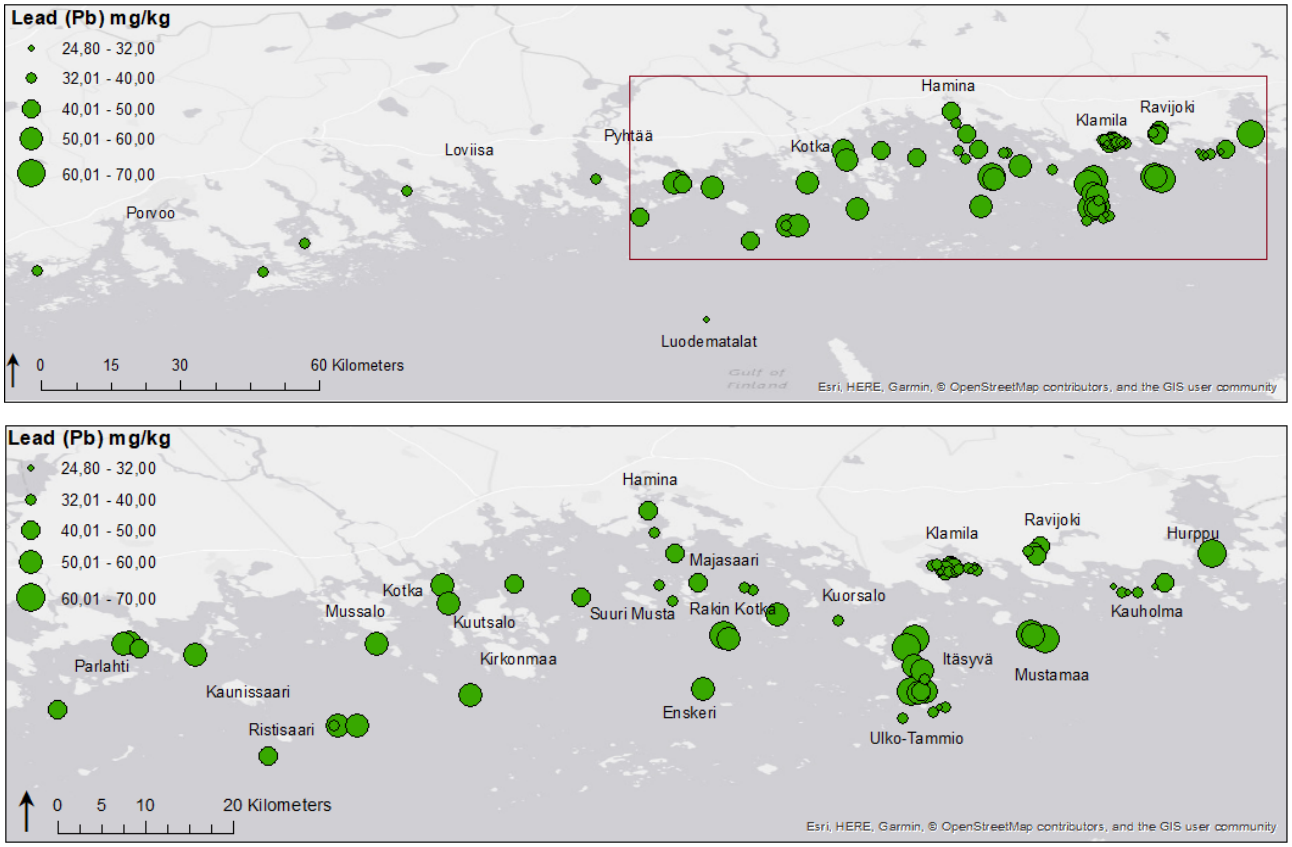

Figure 25. The Pb concentrations appear higher in the east than in the west. The eastern sites show greater variability in the Pb surface sediment concentrations.

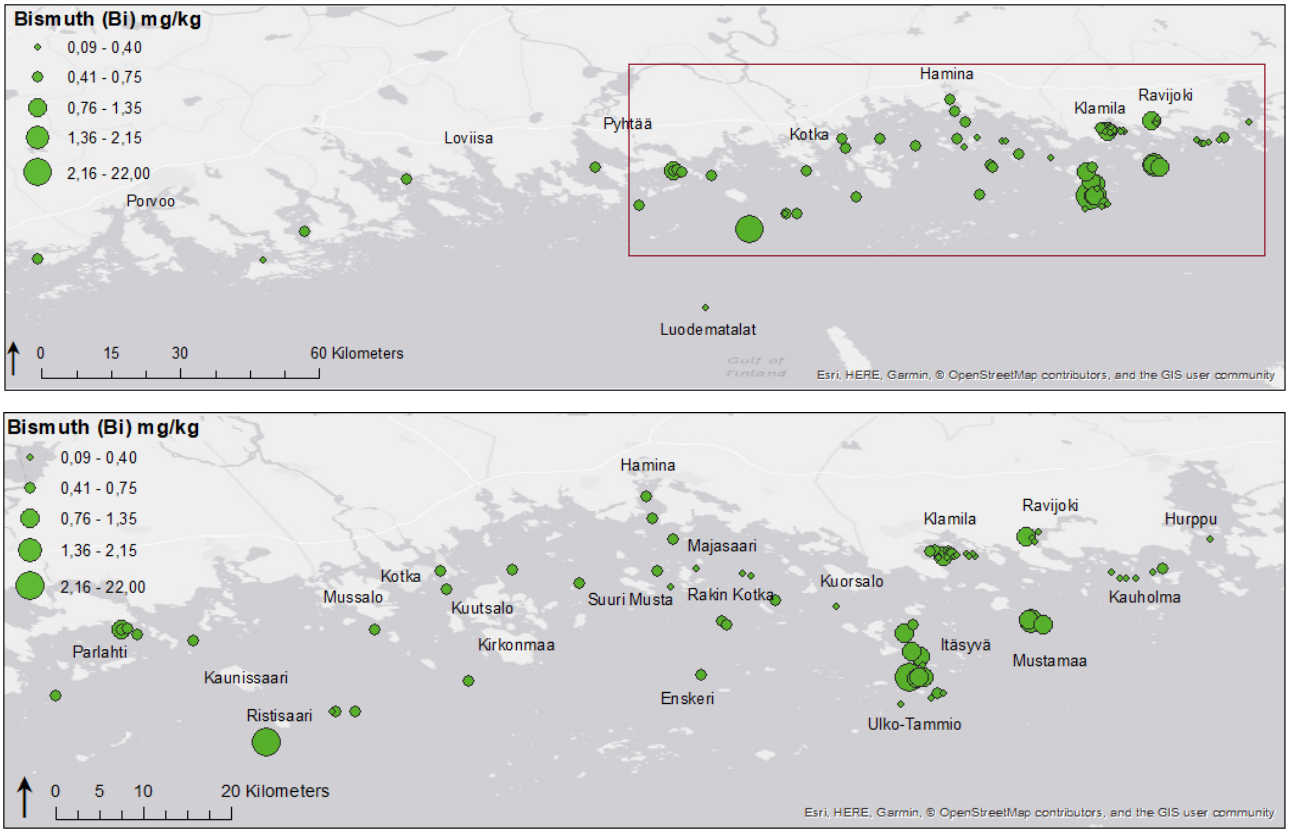

Figure 26. Bi concentrations remained less than 0,75 mg/kg at most sites. The highest concentrations were measured at eastern part of the study area.

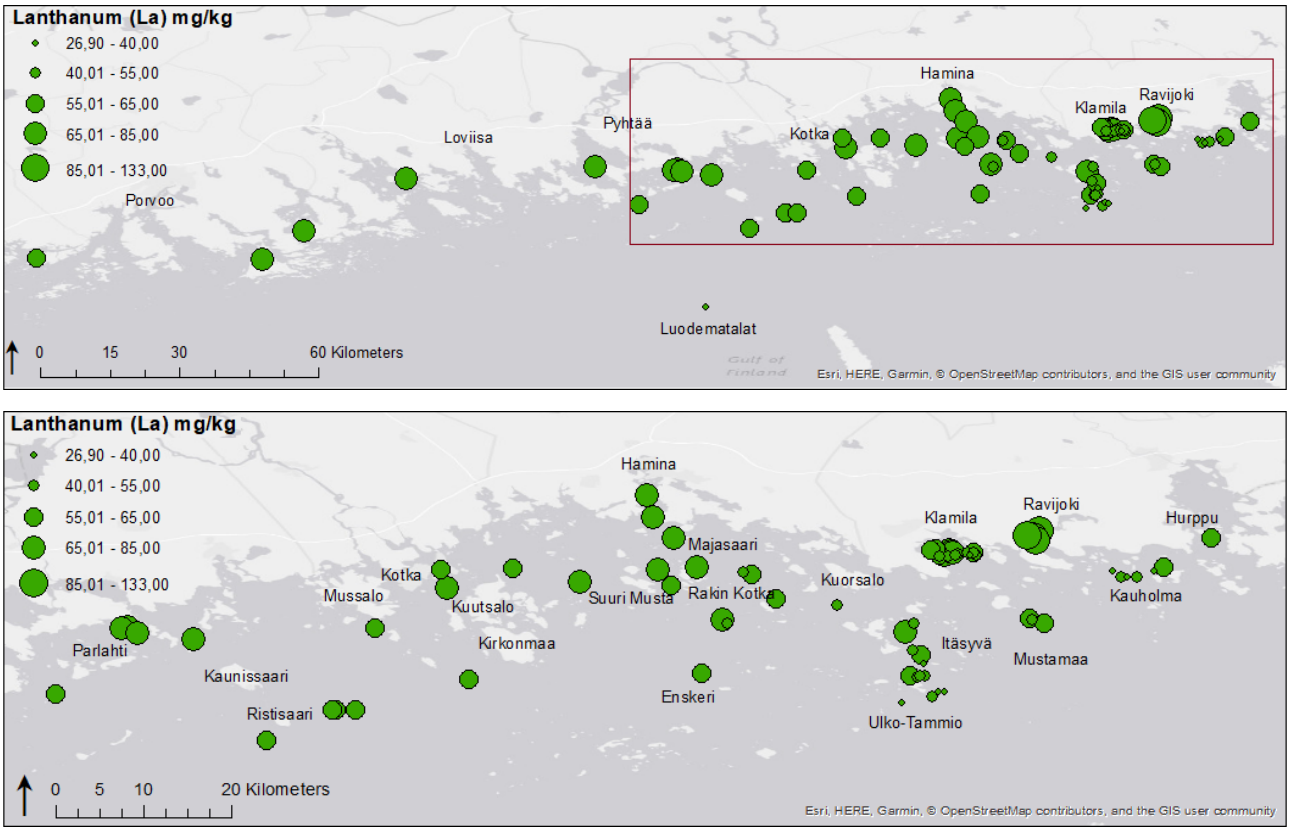

Figure 27. The highest and lowest La concentrations were found in the eastern sites. The concentrations did not show great variability between other sites.

Bi showed rather low concentrations in the study area: the concentrations remained less than 0,75 mg/kg at most sites (Figure 26). The highest Bi concentration was found near Ristisaari (22,00 mg/kg), and concentrations were relatively high in Mustamaa and Itäsyvä, too. The concentrations in Itäsyvä showed variability between the sites.

The lowest La concentrations were discovered in the eastern part of the study area; the concentrations were less than 40,00 mg/kg in Kauholma, Klamila, Ulko-Tammio, Itäsyvä and Luodematalat (Figure 27). The highest concentrations were measured in Ravijoki (above 85,00 mg/kg). La showed the highest and lowest concentrations in the eastern part of the study area, but otherwise remained relatively stable throughout the study area.

6. DISCUSSION

6.1. Trends in the vertical distribution

For most studied elements, the vertical distribution showed a similar trend. The concentrations increased from the bottom of the core until reaching their highest concentrations, after which the concentrations began to decrease towards the most recent sediments (Figures 6 and 7). Using the Cs peak from the Chernobyl accident as a reference, the highest concentrations were dated to the 70's and 80's (Figures 4 and 5). The trend of declining metal concentrations during the last decades, as reported by previous studies from the Gulf of Finland (Vallius et al. 2007, Vallius 2015b), is also seen clearly in the cores MGGN-2013-13 and MGGN-2014-24. However, the metal concentrations have not declined much, or at all, in the core MGGN-2014-22.

Upon the observation of the cores MGGN-2013-13 and MGGN-2014-24, changes in the oxygen conditions were not visible from the surface of the core until the depths of 35 cm and 31 cm, respectively. Both cores had visible laminae, which indicates oxygen depleted and at least seasonally anoxic conditions (Kotilainen et al. 2007). If the metal concentrations were affected mostly due to redox conditions, the reducing conditions would favour the deposition of most metals (Jacobs et al. 1985, Borg and Jonsson 1996, Brügmann et al. 1997, Morford and Emerson 1999, Gubelit et al. 2016, Majithiya et al. 2018). However, the concentrations of most studied elements (V, Cr, Co, Ni, Zn, Cd, Hg, Pb, Bi) decrease towards the recent sediments in these two cores. Hence, the decreasing trend in the metal deposition can be associated with decreasing contamination input, as concluded previously by Borg and Jonsson (1996), rather than the oxygen conditions.

The metal concentrations in the core MGGN-2014-22 have not decreased towards the recent sediments as much as in the other two cores. The difference in the vertical distribution pattern can probably be explained by the oxygen conditions at the sites, combined with the flocculation of metals arriving via river Ravijoki. According to the description of the core MGGN-2014-22, the conditions at the top of the core were oxic; the brown colour has been interpreted to represent oxidized conditions as this colour is linked with solid iron (oxy)hydroxides (Kotilainen et al. 2007). Precipitation of river-borne metals has been reported during estuarine mixing, resulting in the deposition of metals in the bottom sediments of the estuary (Duinker and Nolting 1978), probably due to flocculation of dissolved and colloidal organic matter and Fe/Mn oxyhydroxides (Boldrin et al. 1989). Scavenging of metals by Fe and Mn oxides is a possible explanation for higher metal concentrations in the upper part of the sediment column of the MGGN-2014-22 compared to the other two, since both Fe and Mn are known for their ability to absorb other metals (Burdige 1993, Tessier et al. 1979, Müller 1999,

Vallius and Leivuori 2003). Mn is usually enriched in the oxic zone - Mn is reduced in the sediment column as it is buried and diffused as dissolved Mn (II) upwards and finally, reoxidized at the sediment surface (eg. Sundby et al. 1981, Balzer 1982, Thamdrup et al. 1994), leading to the enrichment at the sediment surface, as seen in the vertical profile of Mn in the core MGGN-2014-22. Ohta et al. (2010) suggested the dissolution and upward diffusion of Mn-bound metals, leading to the surface enrichment as these metals are scavenged by Mn oxides at the sediment surface. Ingri et al. (2014) suggested that the Fe/Mn oxyhydroxide layer could act as a boundary restricting the trace metal exchange between the sediment and the overlying bottom water, resulting in the enrichment of the metals at the sediment surface. However, surface enrichment was not observed with other elements than Mn. The possible effect of bioturbation on the vertical distribution of metals needs to be considered, too. The burrowing biota could disturb the sediment structures and bring older material to the surface (Leivuori and Vallius 2004). If the biota has brought older sediment to the surface, the metal concentrations near the surface could seem higher than they were at the time of deposition.

Some studied elements showed different distribution patterns as described above, the most distinctive ones being the vertical profiles of Mo, La and As. Mo did not show any significant concentration changes in the Ravijoki core, while in the cores MGGN-2013-13 and MGGN-2014-24 the Mo concentrations showed a highly fluctuating pattern. However, the general trend appeared consistent with most metals, even though the concentration peaks were measured higher in the sediment column than with other studied elements. Mo has been used as indicator of redox conditions in many paleoenvironmental studies due to the metal's reduced mobility as oxygen is depleted in the sediments or the water column (Scholz et al. 2018). Mo has also been connected to the Mn cycling; Mo release has been reported upon the dissolution of Mn oxyhydroxides (Chaillou et al. 2008, Scholz et al. 2018), and authigenic enrichments of Mn and Mo have been observed under oxic conditions due to the tendency of Mn oxyhydroxides to absorb Mo (Morford and Emerson 1999). The vertical profiles of Mo did not show similarities with Mn in the core MGGN-2014-22; thus, Mo appeared unaffected and the concentration rather decreased, while Mn concentrations showed a slight increase. The low Mo concentrations could be due to the lack of contamination input through river Ravijoki, and/or the oxic conditions in Ravijoki sediments disfavouring the deposition of Mo in the sediments. In the cores MGGN-2013-13 and MGGN-2014-24, the Mo concentrations showed an increasing trend, which could indicate a possible Mo source from the eastern Gul of Finland. Gubelit et al. (2016) reported elevated Mo concentrations in the water column near the Leningrad Nuclear Power Plant in Neva Estuary. Some Mo could be transported from the east by currents, and the oxygen depleted conditions could have enhanced the deposition of the metal.

Both metal sulphides (Chaillou et al. 2006) and Fe oxides (Haley et al. 2004) have been suggested as carriers of REE's, while the role of Mn oxides has been reported as insignificant (Haley et al. 2004). The La concentrations in the cores MGGN-2013-13 and MGGN-2014-24 showed relatively stable concentrations, while in the core MGGN-2014-22 the La concentration suddenly increased towards the most recent sediments and stayed at relatively high levels. This could indicate that La pollution has not been severe on the Kotka-Hamina sea area. The La distribution pattern in the core MGGN-2014-22 suggests that the La pollution load has increased in the past in Ravijoki and possibly continues, although scavenging by Fe oxides and the effect of flocculation could intensify the La accumulation at the site. Acid sulphate soils could be a possible source of La in the Ravijoki sediments. The change in land use has caused the lowering of the ground water table, leading to the development of acid sulphate soils (Nordmyr et al. 2008).

The vertical profile of As resembles the distribution patterns of most metals in the cores MGGN-2013-13 and MGGN-2014-24, but the Ravijoki core showed a unique pattern (Figure 6). The Fe diagenetic cycle has been reported to control the distribution of As (Chaillou et al. 2003, Widerlund and Ingri 1995). As the sediment is buried, As is reduced to As(III) and released into the porewater when Fe(III) oxides are reduced, followed by the diffusion of As(III) either upwards or downwards in the sediment column (Chaillou et al. 2003). The upward diffusing As is probably trapped in the oxidized surface layer by Fe oxides (Widerlund and Ingri 1995), but some dissolved As is also released to the bottom water (Chaillou et al. 2003). Downward diffusing As is removed from the pore water probably due to coupling with sulphides (Chaillou et al. 2003). Due to this migration of As through the sediment column, the changes of As concentration should be interpreted as changes in the redox conditions rather than changes in the As deposition.

The similarity between the vertical distribution patterns of As and Fe can be seen in the core MGGN-2014-22 from the bottom of the core until the depth of around 16 cm, after which the Fe concentrations began to increase and As concentrations to decrease, except for the slight As concentration increase at the very top of the core. The internal cycling of As has been reported to occur in the upper 10 – 15 cm of the sediment column (Widerlund and Ingri 1995). The Fe concentration decrease from the top of the core downward can be explained by the dissolution of Fe oxides as the conditions become more reducing. The dissolved As upon the reduction of Fe oxides could couple with available sulphide, which is probably seen as an increase of As concentration downcore. The slight enrichment of As in the top 4 cm in the core can probably be explained by the adsorption on Fe oxides in the oxidized surface. However, without the pore water analysis it is difficult to estimate at which extent the As adsorption on Fe oxides occurs in these sediments.

Sb behaviour has been expected to be similar to As based on the position in the periodic table (eg. Filella et al. 2002a), and even though similar behaviour has been reported in river systems, the behaviour of these elements can be very different in estuaries, as Sb tends to be removed from water by flocculation or precipitation (Byrd 1990). Sb has been suggested to accumulate by sinking particles formed in oxic waters (Chaillou et al. 2008), possibly adsorption by Fe oxides (Filella and Williams 2012). In anoxic environments with sulphur available, insoluble stibnite can be formed (Filella et al. 2002b). The vertical distribution pattern of Sb in all three cores showed more similarities with most metals than with As. The Sb pollution appears to have decreased towards present, even in the core MGGN-2014-22; the Sb concentration at the top of the core is relatively close to the value measured at the bottom of the core.

All the metals with defined SQGs exceeded the ISQC level at least at some point in the sediment column in all three cores (Figures 8 – 10). The most recent sediments in all three cores exceeded the ISQC concentrations in case of Cd, Zn, Cu, Pb and As. However, the background value for As is clearly higher than the ISQC level. Taken this into consideration, the level of As pollution does not appear as severe as other elements exceeding the ISQC level in the recent sediments, since the As concentrations were below the estimated background concentration. In addition to As, the ISQC level seems to be set too low at least for Cr and Cu.

The concentrations of Cd, Zn, Cu and Pb still have not declined enough and could pose a severe threat to benthic species. The recent sediments in the core MGGN-2014-22 even exceeded the PEL level in case of Zn, indicating severe pollution in Ravijoki sediments. Other than Zn, only Hg exceeded the PEL level once in the core MGGN-2013-13 at the depth of 29,5 cm. Similar results were presented by Vallius (2015b) for Zn and Hg. The same study reported concentrations higher than PEL levels also for As and Cd. The concentrations of other elements remained below the PEL level in all three cores of this study, including As and Cd.

6.2. Surface sediments

Comparison of the horizontal distribution maps of the elements (Figures 11 – 27) with the correlation coefficients presented in Table 4, seabed substrate map of the area (Figure 3), and the preliminary observations onboard (Kotilainen et al. 2012, Kaskela et al. 2013) indicate a strong influence of the grain size and organic matter in the distribution of metals. Even though the grain size data was available only for the samples taken during the 2012 cruise, the results show that it strongly effects on the distribution of metals. Sandy sediments were described in Kauholma, Luodematalat and Suuri Musta (Kotilainen et al. 2012, Kaskela et al. 2013). In general, low concentrations of studied elements were measured at these sites. Low concentrations were also discovered in Ulko-Tammio, defined as an area with rock and boulders according to the seabed substrate map (Figure 3). Highest concentrations of most studied elements were found in muddy bottoms, such as Ravijoki and Parlahti. All studied metals except Mn were positively correlated with clay, and all but Mn and La showed a strong positive correlation ($r > 70$) with clay. Organic matter, too, appears to influence the distribution of most metals in the study area. Only Mn showed negative correlation with carbon. Co, Cd and Sb showed a moderate positive ($r > 50$), while V, Cr, Fe, Ni, Cu, Zn and Pb showed a strong ($r > 70$) positive correlation with carbon. The lowest correlation coefficients were discovered, respectively, for Mn, Bi, As, La, Mo and Hg.

The horizontal distribution of V was quite even throughout the study area (Figure 12), which is consistent with previous results from the area (Vallius et al. 2007). The background value for V has not been estimated for the area. The V concentrations measured at the bottom of the core were 53,9 mg/kg at depth of 58,5 cm (MGGN-2014-22), 81,5 mg/kg at 70 cm (MGGN-2014-24) and 83 mg/kg at 44,5 cm (MGGN-2013-13). Even though the background value cannot be directly estimated from these three cores, the surface sediments clearly exceeded these values both in the eastern and western parts of the study area. Concentrations >85,6 mg/kg were measured in Mustamaa, Itäsyvä, west of Loviisa and west of Porvoo. The SQGs for V are not available. High V concentrations at the western sites, where some inconsistency in the distribution of V and carbon was observed, are probably related to Fe; adsorption of V on Fe surfaces has been previously described (Morford and Emerson 1999). The correlation coefficient between these two metals is high (0,89), suggesting they are enriched at same sites.

Evenly distributed concentrations have been reported for Cr before in the sediments of the Gulf of Finland (Vallius et al. 2007). In the surface sediments of the study area, Cr showed high concentrations both in the eastern and western sites, and slightly lower concentrations in the middle

(Figure 13). The mean (55,2 mg/kg) and median (62,8 mg/kg) values both exceeded the ISQC level (52,3 mg/kg), but were below the background level of 69,4 mg/kg estimated by Vallius (2007) and the PEL level (160 mg/kg). However, the background level was exceeded at 27 sites, including most sites in the western part of the study area.

The both mean (11,5 mg/kg) and median (12,0 mg/kg) values of Co were below the background value of 15,6 mg/kg. The horizontal distribution pattern of Co was quite even (Figure 16), as reported earlier by Vallius et al. (2007). The background level was, however, exceeded at 16 sites, including Itäsyvä, Mustamaa, Ravijoki and the western sites.

Even though most metals, including Cr and Co, most likely occur in the sediment under reducing conditions, favoured deposition of Cr and Co under oxic conditions has been reported based on the horizontal distribution maps in the Gulf of Finland (Vallius 1999a, Vallius and Leivuori 1999). This behaviour could at least partly explain the relatively high concentrations of Cr and Co near the coast in the western parts of the study area. Enhanced Co values in the sediment could be related to the the fact that Co (III) is more strongly sorbed than Co (II) (Ingri et al. 2014). Cr reduction has been reported even in the presence of oxygen (Markelova et al. 2018) - Cr can be reduced from Cr (VI) to Cr (III) by the Fe (II) in clay minerals, after which it can be precipitated and deposited as $Cr(OH)_3$ (Kwak et al. 2018). Once reduced, Cr (III) seems to be stable even in oxygenated waters – the presence of oxygen had no measurable effect on the oxidation of Cr (III) to Cr (VI) (Magar et al. 2008, Markelova et al 2018).

Cu, Zn, Cd and Ni have been described highly mobile in oxic conditions and are transported to the north-eastern GOF from Neva estuary, but also from Vyborg Bay, the Kymi river and cities such as Kotka and their environs (Vallius 1999a). Of these metals, only Ni showed lower median value (32 mg/kg) than the background level (34,9 mg/kg). However, many sites both in the eastern and western parts of the study area exceeded the background level. The horizontal distribution pattern of Ni was relatively even; similar results have been earlier reported by Vallius et al. (2007). The distribution pattern correlates quite well with the carbon distribution, which is also indicated by the high correlation coefficient of 0,77 between these two elements.

The distribution pattern of Cu showed higher concentrations in the east (Figure 18). Values above 60 mg/kg were measured in Itäsyvä and Mustamaa. Similar results were reported by Vallius et al. (2007); highest concentrations (> 60 mg/kg) were located near the border of Finland and Russia, suggesting transport from the east. High Cu concentrations were also measured in Parlahti, which could indicate an additional source from River Kymi. Both the mean (40,6 mg/kg) and median (47,4 mg/kg) values

exceeded the ISQC level (18,7 mg/kg) and the background level (30,2 mg/kg) but were below the PEL level (108 mg/kg). Even though the correlation coefficient (0,90) and the horizontal distribution maps indicate that Cu and carbon are enriched at same sites, the Cu mean and median values clearly exceeded the background level suggesting anthropogenic sources for Cu.

The Zn distribution pattern was relatively even (Figure 19). Zn concentrations were positively correlated with C (r = 0,77) and clay (r = 0,95), indicating very strong adsorption on clay minerals and a good correlation with organic matter. Sediments at Itäsyvä and Mustamaa showed high concentrations (> 200 mg/kg) that exceeded the background value of 120 mg/kg. From the same area, Vallius et al. (2007) reported similar results; a slight increase of Zn concentrations near the border of Finland and Russia, but otherwise Zn showed quite even distribution. The Ravijoki sediments also showed very high concentrations, and the highest Zn concentration (310 mg/kg) was measured here. This suggests that Zn could have another source arriving from Ravijoki, but the possibility of biota bringing older sediment to the surface and thus affecting the metal distribution cannot be ruled out either in the oxidized Ravijoki sediments. The mean (164 mg/kg) and median (169 mg/kg) values for Zn exceeded both the background value and ISQC level (124 mg/kg) but were below the PEL limit (271 mg/kg). However, three individual values exceed the PEL level. Two of these (310 and 285 mg/kg) were measured in Ravijoki, and one (277 mg/kg) south-east of Rakin Kotka.

The reduction of particulate Mn has been suggested to increase the amount of dissolved Mn under anaerobic conditions (Duinker et al. 1978), leading to the depletion of Mn in the sediments. Jung et al. (1996) studied the behaviour of Mn and Cu in anoxic sediments and suggested that the depletion of Mn in sediments and the enrichment of Cu is due to the escape of dissolved Mn ions from the sediment to the water column, while the Cu ions are coupled with sulphide ions and precipitated as copper sulphides. Previous studies have suggested that the dissolved forms of many metals such as Fe, Co, Cd, Cu and Zn may be controlled by sulphide coprecipitation in low-oxygen conditions, whereas Mn is not necessarily precipitated as sulphides (Brügmann et al. 1997). Low correlation coefficient between Mn and most other elements could be explained by the metal sulphide formation. Itäsyvä surface sediments showed high concentrations with most studied elements, but low Mn concentrations (Figure 14); hence, oxygen-depleted conditions could prevail here, which could explain the different behaviour of Mn at the site.

Since both Mn and Fe form oxides, their deposition would be expected under oxic conditions, such as in Ravijoki. However, these surface sediments showed relatively low Mn and high Fe concentrations (Figures 14 and 15). Sediments were also relatively high in the concentration of carbon, which could explain the relative depletion of Mn in these surface sediments. When organic

matter accumulation is sufficiently high, the Mn reduction is favoured over Mn oxidation, leading to the escape of Mn from sediment to the overlying water column (Aller 1994). Vertical distribution pattern of Mn (Figure 6) indicates Mn shuttling through the sediment column, reduced Mn diffusing upwards and at least some of it probably oxidized at the sediment surface. Due to its slow oxidation rate (Balzer 1982), the Mn^{2+} is relatively persistent in the estuarine water and could be transported to considerable distance from its source before oxidizing and accumulating in the sediments (Åström et al. 2012). Both Canfield et al. (1993) and Sundby et al. (1981) suggested that escaped Mn^{2+} from the near coastal sediment can be redeposited in the deeper areas of the basin. Under the conditions in which the reductive dissolution of Mn results in the escape of Mn^{2+} from the sediment, Fe^{2+} has been suggested to stay in the sediment due to the precipitation of non-sulfidic ferrous compounds and adsorption on the sediment (Thamdrup et al. 1994). Hence, the escaped Fe^{2+} would be balanced by re-sedimentation of Fe oxides, whereas more slowly formed Mn oxides could be transported by currents and deposited somewhere else. Based on the horizontal distribution map, it seems that higher Mn concentrations were measured further away from the coast.

The surface sediments of the study area were severely affected by Cd. The mean (1,27 mg/kg) and median (1,11 mg/kg) values of Cd were clearly above the background level of 0,16 mg/kg and exceeded the ISQC level (0,7 mg/kg) but were below the PEL level (4,2 mg/kg). Even the lowest Cd concentration, 0,17 mg/kg, exceeded the background level, and most of the sites exceeded the ISQC level, too; only 11 sites had Cd concentrations less than 0,7 mg/kg. The horizontal distribution of Cd showed an increasing trend towards east (Figure 22). This distribution pattern supports the hypothesis that the main Cd pollution load would arrive from the east, as suggested earlier by Vallius and Leivuori (1999). According to Vallius (2011), the Cd distribution appears to correlate with the anthropogenic Cd available rather than any geological provinces. The Cd concentrations were lower in the sites near the cost; the eastern transport of contaminants would result in lower metal concentrations in the coastal areas, as these off-shore currents pass by the areas near the coast (Vallius et al. 2007). Other sites with low concentrations can be associated to the low carbon and clay fraction in the sediment (Ulko-Tammio). Even though the Cd enrichment has been reported as a good indicator of the presence of sulphide (Chaillou et al. 2002), and accumulation as CdS during anoxic periods caused by the high rate of organic matter decomposition has been reported (Pohl et al. 1998), the horizontal distribution pattern in this area is most likely affected by the anthropogenic sources rather than oxygen conditions. Cd concentrations in the Kotka-Hamina sea area and the western part of the study area were generally lower than the carbon concentrations, while generally higher concentrations were measured in the east and near Ristisaari. These inconsistencies with the carbon

distribution in the surface sediments most likely indicate the eastern-driven anthropogenic origin of Cd.

Arsenic tends to bond with organic matter, clay, oxides and hydroxides, and oxygen-depleted conditions support the precipitation of arsenic as arsenic sulphides (Leivuori and Vallius 2004). As expected, arsenic shows high correlation with clay (r = 0,86), but lower with C (r = 0,29), which indicates that organic matter has lower influence in the accumulation of As than with most studied elements. Both the mean and median values exceeded the ISQC level of 7,24 mg/kg but were below the background level of 16,4 mg/kg estimated by Vallius (2007) and the PEL limit of 41,6 mg/kg. In the studied surface sediments, the distribution pattern of As did not show any clear trend (Figure 20). Most As concentrations were rather low (median value was 9,52 mg/kg and mean 10,0 mg/kg), but high concentrations were measured at some sites; most high As concentrations were related to the water depth of over 30 metres, but the highest concentration (48,5 mg/kg) was measured at water depth of 19 metres near Rakin Kotka. According to Kotilainen et al. (2007), anoxic surface sediments were not found shallower than 25 metres, but the laminated sediment structure in shallow depths was suggested to be caused by seasonally depleted oxygen conditions. The cores MGGN-2013-13 and MGGN-2014-24 had black surfaces and visible laminae, and these samples were taken near the site with maximum As concentrations; taken into consideration their distance, it is likely that anoxic conditions prevail at this site, too, at least seasonally, which favours the As precipitation as sulphides.

As showed the highest correlation coefficients with Fe (r = 0,66), Mo (r = 0,64) and Mn (r = 0,63), which indicates that As could be linked with both Fe and Mn oxides. It needs to be considered, though, that both As and Fe tends to bond with sulphur; the moderate positive correlation coefficient between As and Fe could be partly due to both elements' tendency to bond with sulphur under oxygen-depleted conditions. In the oxic and shallow Ravijoki sediments, As did not show very high concentrations. Even in oxic conditions, some As may escape the sediment to the overlying bottom water as dissolved As, but is most likely immediately trapped by carriers such as Fe oxides and redeposited (Chaillou et al. 2003). The relatively low As concentrations suggest that As is not that strongly sorbed by Fe oxides in these sediments, or the escaped As from the sediment is trapped by carriers that are deposited somewhere else, such as Mn oxides.

The mean value of Mo was 2,21 mg/kg and median 1,27 mg/kg. The background level or SQGs have not been estimated for Mo, but usually Mo does not show high concentrations in modern marine sediments (Vallius 2011). The Mo concentrations measured at the bottom of the cores were 1,4 mg/kg at 44,5 cm (MGGN-2013-13), 2,24 mg/kg at 58,5 cm (MGGN-2014-22) and 5,76 cm at 70 cm (MGGN-2014-24). The distribution pattern of Mo showed higher concentrations in the east than in

the west, which is consistent with the earlier observations by Vallius (2011). Mo is strongly controlled by local physical and chemical conditions, which makes the input source less important (Vallius 2011), as Mo is clearly enriched in the sediment under anoxic conditions (Morford and Emerson 1999). Mo can deposit under oxic conditions, too; absorption on Mn oxides/hydroxides has been reported (Morford and Emerson 1999, Chaillou et al. 2008, Ohta et al. 2010, Bauer et al. 2018). Mo showed highest correlation coefficient (0,52) with Mn and Sb, which suggests that Mo could be linked with Mn. Both Mo and Mn showed relatively low concentrations with surface sediments near the coast (Figures 14 and 21); the slowly oxidizing Mn could scavenge Mo in the water column before depositing.

High Mo concentrations in Itäsyvä and Mustamaa could indicate oxygen depleted conditions. The observed trend in the horizontal distribution could be partly explained by the oxygen conditions of the seafoor, but some high Mo concentrations are probably derived from anthropogenic sources from the east, as suggested by Vallius (2011) earlier. The concentrations at the anoxic surfaces of the cores MGGN-2013-13 and MGGN-2014-24 were 5,3 mg/kg and 5,4 mg/kg, respectively, and most sites near the coast, where oxic conditions are expected, showed lower concentrations than these, suggesting favoured Mo deposition under oxygen depleted conditions. The vertical distribution pattern observed from the cores support the assumption of at least partly eastern-driven Mo source; the Mo concentrations in the cores MGGN-2013-13 and MGGN-2014-24 began to increase in the past, but in the upper 10 centimetres the trend alters, and the concentrations appear to decrease towards the surface of the core. Even though the concentration increase could be linked to the change in the conditions of the seafloor indicated by the change from mud to laminated sediment, the change in the upper part of the sediment column cannot be explained by the change in the oxygen conditions of the seafloor. Hence, at least some Mo is probably transported from the east by currents, and the oxygen depleted conditions could have enhanced the deposition of the metal.

Usually, the Sb concentrations in sediments are in the order a few μg/g, and higher concentrations are related to anthropogenic sources (Filella et al. 2002a). The Sb concentrations in the study area varied from 0,15 mg/kg to 2,67 mg/kg. Even though the concentrations were not high, Sb showed higher concentrations in the east than in the west, and lower concentrations near the coast (Figure 23). The correlation coefficient of 0,52 between Sb and Mo could indicate similar source, supporting the eastern origin of the metals. Byrd (1990) associated Sb with particles – the removal of Sb from water via flocculation or precipitation. Positive correlation coefficient with clay ($r = 0,76$) indicates that adsorption on clay minerals is important. According to Filella and Williams (2012), adsorption to natural organic matter appears to be limited, but Fe oxyhydroxides are most likely important in Sb

binding (Filella and Williams 2012). The correlation coefficient between Sb and Fe (r = 0,45) could indicate adsorption on Fe oxides, but on the other hand, Sb showed as high or even higher correlation coefficients with other metals. Moderate positive correlation coefficient with C (r = 61) suggests that organic matter might be more important carrier for Sb than Fe oxides. However, under anoxic conditions and abundant S available, insoluble stibnite (Sb_2S_3) formation can occur, and high carbon content in the sediment could also suggest oxygen-depleted conditions, which could favour stibnite formation.

Hg showed highest concentrations (0,411 mg/kg) in the outlets of river Kymi (Figure 24), which suggests the river as the primary source of Hg. Relatively high concentrations were measured at sites in Mustamaa and Itäsyvä, too. Similar results were presented by previous studies from the north-eastern Gulf of Finland (Vallius 2011, Vallius et al. 2007). The relatively high concentrations in the east, compared to western sites of the study area could suggest another Hg source in the east, as speculated by Vallius et al. (2007) earlier. The mean (0,12 mg/kg) and median (0,11 mg/kg) values for Hg were below the ISQC level, but clearly exceeded the background value of 0,017 mg/kg. Hg surface sediments were positively correlated with clay (r = 0,88), silt (r = 0,45) and C (r = 0,47), which indicates strong adsorption on clay minerals, but also organic matter and silt play a role in the distribution of Hg in the study area.

Pb surface sediments showed high positive correlations with clay (r = 0,91) and carbon (r = 0,72), which indicates that both have an impact on the distribution of Pb. The mean (43,8 mg/kg) and median (41,7 mg/kg) values exceeded the ISQC value (30,2 mg/kg) and the background concentration of 24,0 mg/kg but are below the PEL level (112 mg/kg). Vallius et al. (2007) did not report any clear trend for Pb in the surface sediments. In the study area, Pb concentrations appeared highest in the eastern part of the study area (Itäsyvä, Mustamaa), and clearly higher in the eastern part of the study area compared to the western part (Figure 25). This distribution pattern of clearly higher concentrations in the east could indicate a possible Pb source derived from the eastern Gulf of Finland. High concentrations were also measured near Kotka and Parlahti, which suggests additional source via river Kymi.

Like any other chemical element, Bi enters the waters through natural (rock weathering, soil runoff) and anthropogenic sources, such as pharmaceuticals, cosmetics and metallurgical additives (Filella 2010). Atmospheric deposition of anthropogenic Bi, such as fossil fuel combustion, has been documented on global scale (Liu et al. 2011). Ingri et al. (2014) reported scavenging of Bi by particles, also biogenic. Bi had a positive correlation coefficient with carbon, but compared to the other studied elements, the concentration coefficient of 0,18 was much lower than with other elements. High

positive correlation coefficient with clay (r = 87) indicates the significance of the adsorption by clay minerals. Bi showed relatively even concentrations at most sites (Figure 26). The highest concentration was measured south-west of Ristisaari, and relatively high concentrations were measured in Itäsyvä and Mustasaari, too. The distribution pattern of Bi most likely indicates low pollution load from the mainland. The highest Bi concentrations could be, at least partly, derived from the eastern parts of the Gulf.

High and moderate positive correlations with silt (r = 0,74) and clay (r = 0,58) suggest that La is adsorbed on the surfaces of both. Previously, Hermann et al. (2016) reported high affinity of La to sediments, enriched in the fine grain size. With carbon, La showed lower correlation coefficient (r = 0,38), indicating that adsorption by silt and clay are more important factors in the La distribution. The background concentration for the area or the Canadian SQGs have not been assessed for La, but both mean (60,09 mg/kg) and median (59,5 mg/kg) values of La exceeded the maximal permissible concentration of 36,9 mg/kg estimated by Hermann et al. (2016). However, the estimated concentration should be interpreted with care, since it is based on relatively small number of studies and the toxic species of La are influenced strongly by environmental conditions, which are specific for each site (Hermann et al. 2016). In addition, the bedrock in the study area consists mainly of rapakivi granite, and this type of granite typically has higher concentrations of REE's than typical granites (Rämö et al. 1998, 274). Acid sulphate soils have been suggested as an important source of metals in estuaries, including REE's (Åström et al. 2012, Nordmyr et al. 2008), and could be a possible source for La. Recently, La emissions have been reported to increase due to its' use in modern technologies (Hermann et al. 2016). Mixing processes in estuaries remove dissolved La, which evidently leads to the La sedimentation (Herrmann et al. 2016). Dissolved REE removal in the estuaries can be caused by many factors: co-precipitation with oxyhydroxides (Al, Fe), complexation with organic substances and sorption to particles (Åström et al. 2012). The La horizontal distribution pattern appeared relatively even (Figure 27), mainly influenced probably by the grain size distribution.

7. CONCLUSIONS

The vertical profiles of seabed sediments show that the concentrations of most studied elements have decreased during the last decades in the north-eastern Gulf of Finland. The concentration decrease in Ravijoenlahti is not that obvious than in the profiles shown by two other cores. Instead of a constant decrease, the concentrations decline only slightly, and the concentrations at the top are clearly higher than the concentrations measured at the bottom of the core. The observed difference in the behavior of the studied elements is probably due to the oxygen conditions of the seafloor. The core description indicated oxidized conditions in Ravijoenlahti, whereas anoxic conditions were found in the proximity of Rakin Kotka. When oxidized conditions prevail, metals and other elements are efficiently scavenged by Fe and Mn oxides and eventually accumulate in the sediment. In addition to this, bioturbation may have disturbed the vertical profiles in the sediments of Ravijoenlahti and brought older sediment to the surface, elevating the contaminant levels in the upper sediment core.

Most studied elements showed high positive correlations with carbon in the surface sediments, indicating that carbon strongly effects the distribution of metals. The grain size was also an important factor - the metals showed higher concentrations in muddy areas, whereas lower concentrations were found in areas where finer sediment fraction was depleted. Mn showed a considerable exception to this, showing negative correlations with both the finer sediment fraction and carbon. In the areas with high organic matter accumulation, Mn reduction overcomes Mn oxidation, leading to the dissolution of Mn. The horizontal distribution map of Cd showed a quite clear trend in the metal distribution, with higher concentrations in the eastern part of the study area, indicating that the main Cd pollution load is brought by currents from the eastern part of the Gulf. The horizontal distribution maps of Hg, Mo, Cu, Zn also showed a possible pollution source in the east. The deposition of As and Mo was probably enhanced by oxygen-depleted conditions on the seafloor and may have enhanced the deposition of other sulphide forming metals, too. The river Kymi still appears to act as a source for Hg and Pb, and possibly for Cu, too.

Even though the median values of any element with defined SQGs (Cd, Cr, Zn, Cu, Hg, Pb and As) in the surface sediments did not exceed the PEL level, the highest concentrations of Zn and As exceeded this level. The ISQC level in the surface sediments was exceeded by the median values of all other elements with defined SQGs except for Hg. However, the maximum concentration of Hg clearly exceeded the ISQC level, indicating that all these metals and As could locally pose a severe threat to benthic species. It needs to be considered, though, that these SQGs were defined for another area, and the results should be interpreted with caution, especially in the case of As, Cu and Cr, since

the ISQC level of these elements seems to be set too low for the study area. Even if the concentration at the sediment surface was at acceptable levels, some metals (Cd, Zn, Cu and Pb) clearly exceeded the ISQC levels in the upper 20 cm in the sediment column and could cause adverse biological effects to the species burrowing in the sediment. The situation is especially severe in the case of Zn, since the metal exceeded even the PEL level in the oxidized core of Ravijoenlahti.

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